# LABORATORY METHODS FOR DETERMINATION OF PHYSICOCHEMICAL CHARACTERISTICS OF PRECIPITATION

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## PREFACE

The establishment of the Quebec precipitation-sampling network presented our laboratory with a new set of problems: how to analyse samples in which the ion concentrations of interest would commonly fall below the detection limits of our usual methods; how to analyse all the parameters of interest with only 200 mL of sample; and how to process all the samples with our limited staff. We solved these problems by adopting a new analytical approach, automated ion-exchange determination with conductometric detection.

The first two sections of this document provide a detailed description of how the ion-exchange technique is used to determine total ion concentration, total alkalinity, and concentrations of hydrogen, chloride, nitrate, and sulfate ions. The third section describes methods of measuring and calculating pH of acid precipitation. Subsequent sections deal with sample-storage requirements, interferences in the ion-exchange analyses, and quality control of the results.

This document was written by Marcel Faucher, who developed the methods described in it. The computer program used with these methods was written by Jean-Claude Ferland. Page layout and typing were done by Claire Audet.

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## I. AUTOMATED METHODS OF PRECIPITATION ANALYSIS BY ION EXCHANGE WITH CONDUCTOMETRIC DETECTION

A- Determination of total ion concentration less hydrogen-ion concentration

B- Determination of total ion concentration less concentration of alkaline ions ($OH^-$, $CO_3^{--}$, $HCO_3^-$)

C- Determination of total ion concentration less concentration of alkaline ions ($OH^-$, $CO_3^{--}$, $HCO_3^-$) and chloride ions ($Cl^-$)

D- Determination of total ion concentration less concentration of alkaline ions ($OH^-$, $CO_3^{--}$, $HCO_3^-$), chloride ions ($Cl^-$), and nitrate and nitrite ions ($NO_3^-$ + $NO_2^-$)

I-A

# DETERMINATION OF TOTAL ION CONCENTRATION

# LESS

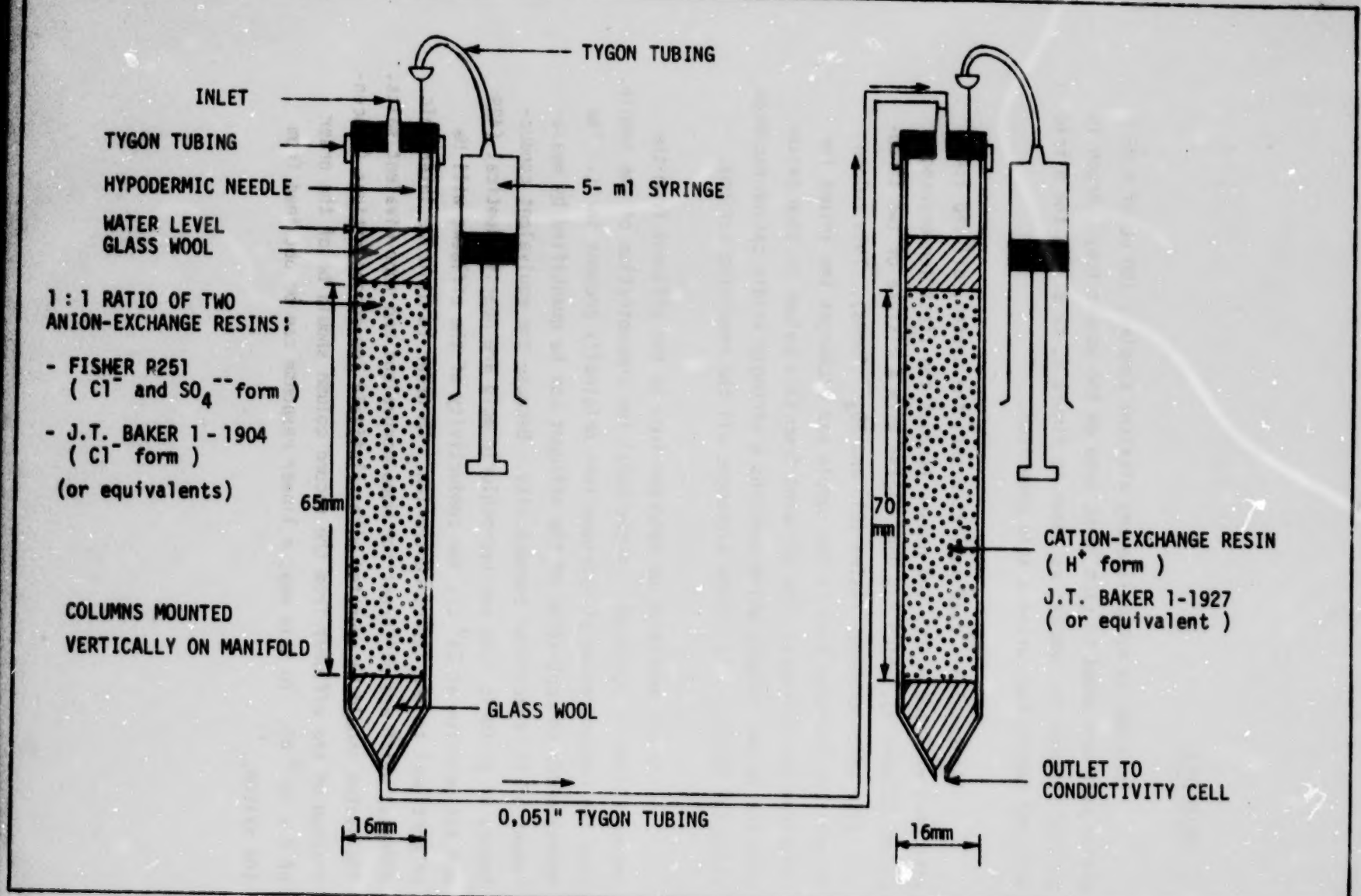
# HYDROGEN-ION CONCENTRATION

## 1. PRINCIPLE

In order to neutralize any alkaline samples, 100 µL of 0.01 N nitric acid are added to each 15-mL tube on the sample tray. Argon is bubbled through the samples as shown in figure 2, to mix in the nitric acid and remove the carbonic acid generated.

The sample is then aspirated into the system, diluted 1:4 with demineralized water, and passed through the first ion-exchange column (figure 1), which has been packed with a mixture of two strongly basic anion-exchange resins ($Cl^-$ and $SO_4^{--}$ forms). This column absorbs the hydrogen ions in the sample and exchanges the anions for chlorides and sulfates. The effluent from this column is then passed into the second column, which contains a strongly acidic cation-exchange resin ($H^+$ form). This column exchanges all the remaining cations.

The concentration of hydrogen ions in the effluent from the second column is equivalent to the total ion concentration of the sample, less the concentration of hydrogen ions originally present in it. The hydrogen-ion concentration of the effluent can be quantified by measurement of its electrical conductivity. Because the equivalent conductances of sulfuric acid and hydrochloric acid are nearly identical (429 and 426 µmhos/cm at $25^o$ C), the conductivity of the effluent will be proportional to the ion concentration. In order to minimize interionic effects, which are different for mono-monovalent and mono-divalent salts, the system should be operated with relatively low concentrations (concentration of the effluent from the second column should be of the order of $5 \times 10^{-5}$ N). In this way, a linear response can be obtained from the system.




ION-EXCHANGE COLUMNS FOR METHOD I-A

FIGURE 1

Because conductivity varies approximately 2% per degree Celsius, the liquid in the conductivity cell must be kept at constant temperature. The laboratory should therefore prepare sufficient dilution water for a full day's operations far enough in advance for it to come up to room temperature. Given the additional time the sample spends in the system before reaching the cell, a temperature-stabilizing bath for the cell should then not be essential.

## 2. STORAGE OF SAMPLES

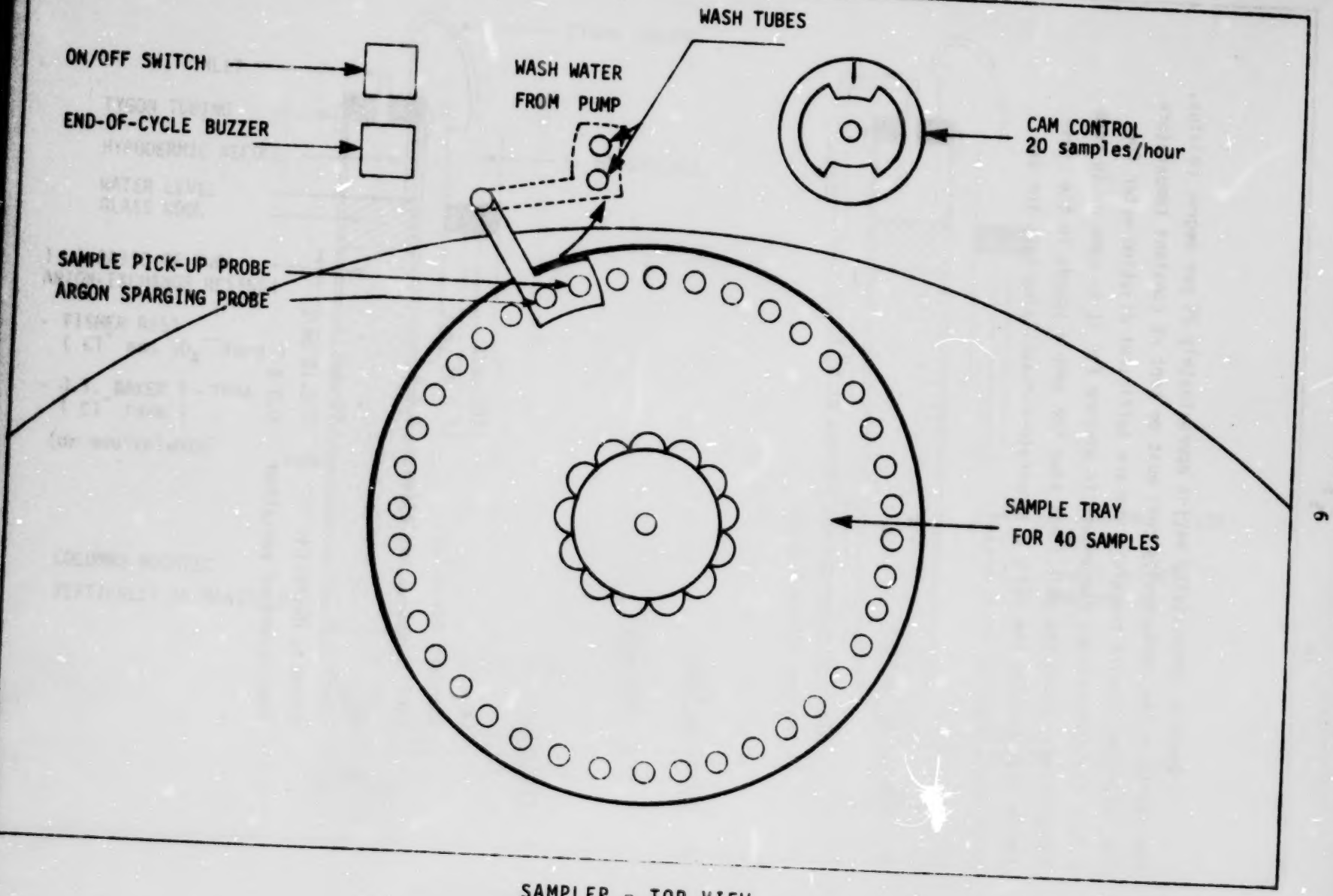
- Store in polypropylene bottles at $5^{o}$ C.
- Analyse within 7 days.

## 3. OPERATING RANGE

2 - 200 µe/L

## 4. PRECISION

| | |
|---|---|
| - Level | 100 µe/L |
| Standard deviation | ± 0.45 µe/L |
| Coefficient of variation | 0.4 % |
| - Level | 40 µe/L |
| Standard deviation | ± 0.12 µe/L |
| Coefficient of variation | 0.3 % |




SAMPLER - TOP VIEW

FIGURE 2

## 5. REAGENTS

5.1 0.01 N nitric acid

5.2 Strongly basic anion-exchange resin, $Cl^-$ and $SO_4^{--}$ form, mesh size 16-50 (Rexyn 201 [ Fisher catalogue No R251 ] or equivalent)

5.3 Strongly basic anion-exchange resin, $Cl^-$ form, mesh size 20-50 (Dowex 1-X8 [ J T Baker catalogue No 1-1904 ] or equivalent)

5.4 Strongly acidic cation-exchange resin, $H^+$ form, mesh size 20-50 (Dowex 50W-X8 [ J T Baker catalogue No 1-1927 ] or equivalent)

5.5 Argon with two-stage pressure regulator

## 6. STANDARDS

6.1 1.0 N ammonium sulfate

6.2 1.0 N nitric acid

6.3 Prepare an intermediate solution containing 10 000 µe/L nitric acid and 10 000 µe/L ammonium sulfate

6.4 Prepare a set of standard solutions containing this intermediate solution in concentrations ranging from 40 to 400 µe/L.

Note: A solution containing equal concentrations of ammonium sulfate and nitric acid is used as the standard in order to replicate the major ions in acid precipitation. Thus the same set of standards can be used to calibrate the systems for all four methods described in this text.
Though 40 to 400 µe/L is the actual range of total ion concentrations of the standards, their effective calibration range in method I-A will be 20 to 200 µe/L, because this method determines total ion concentration less the concentration of hydrogen ions.

## 7. APPARATUS

7.1 Technicon Sampler IV (figure 2)

7.2 Technicon Proportioning Pump III

7.3 Manifold (figure 3)

7.4 Radiometer CDC114 flow-through conductivity cell, cell constant = .66 $cm^{-1}$

7.5 Radiometer CDM3 conductivity meter

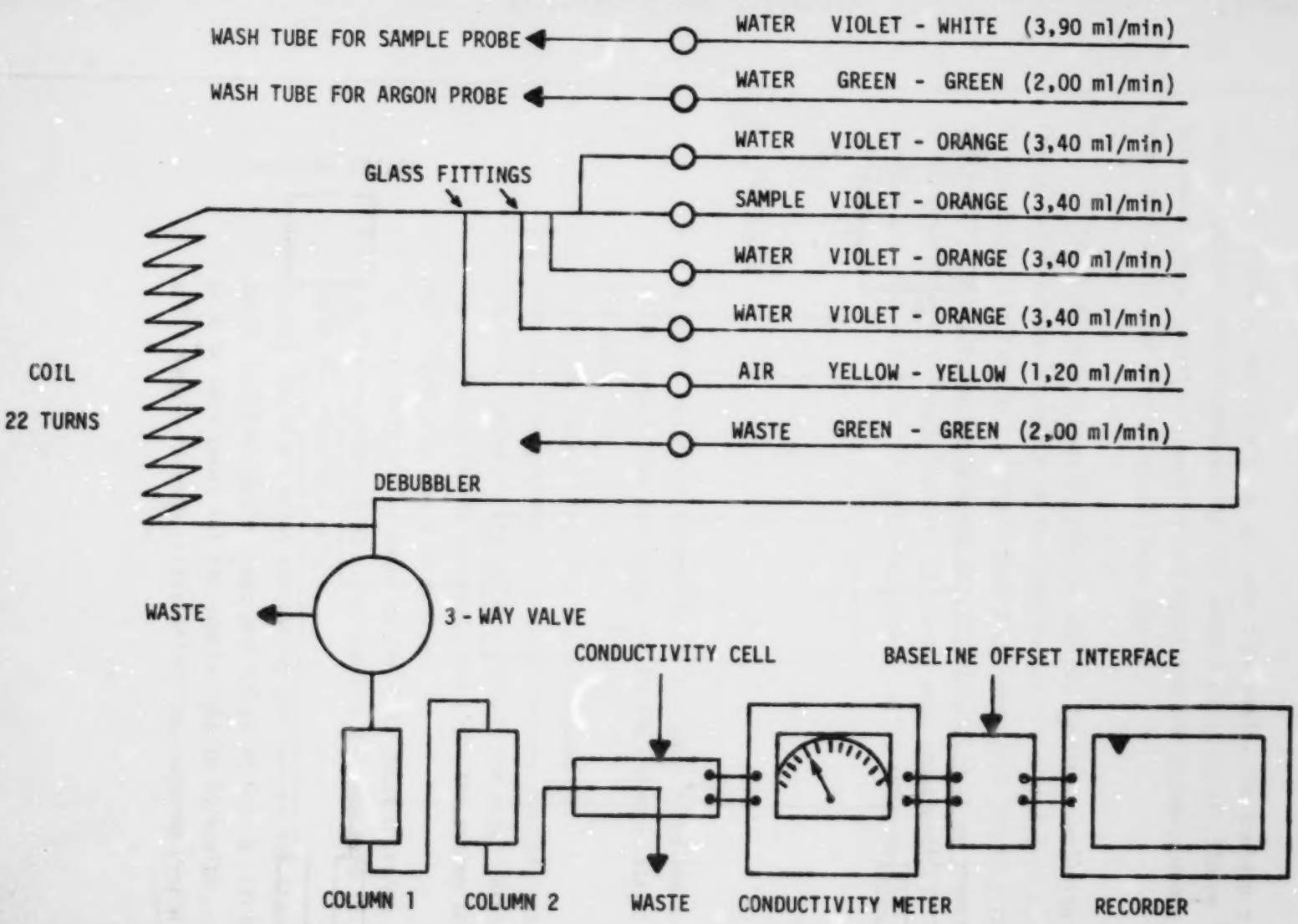
7.6 Baseline offset interface (figure 4)

Note: The signal output from the conductivity meter is 0 to -1000 mV full scale. When the system is run on the 0-15 µmhos/cm range, the baseline response is approximately -250 mV. The interface unit is used to offset the baseline signal so that the recorder receives a 0 mV signal. Though this unit is not essential, it facilitates calibration by preventing the recorder from amplifying the baseline along with the signal from the standards.

7.7 Radiometer REC80 Servograph recorder with REA112 high-sensitivity unit

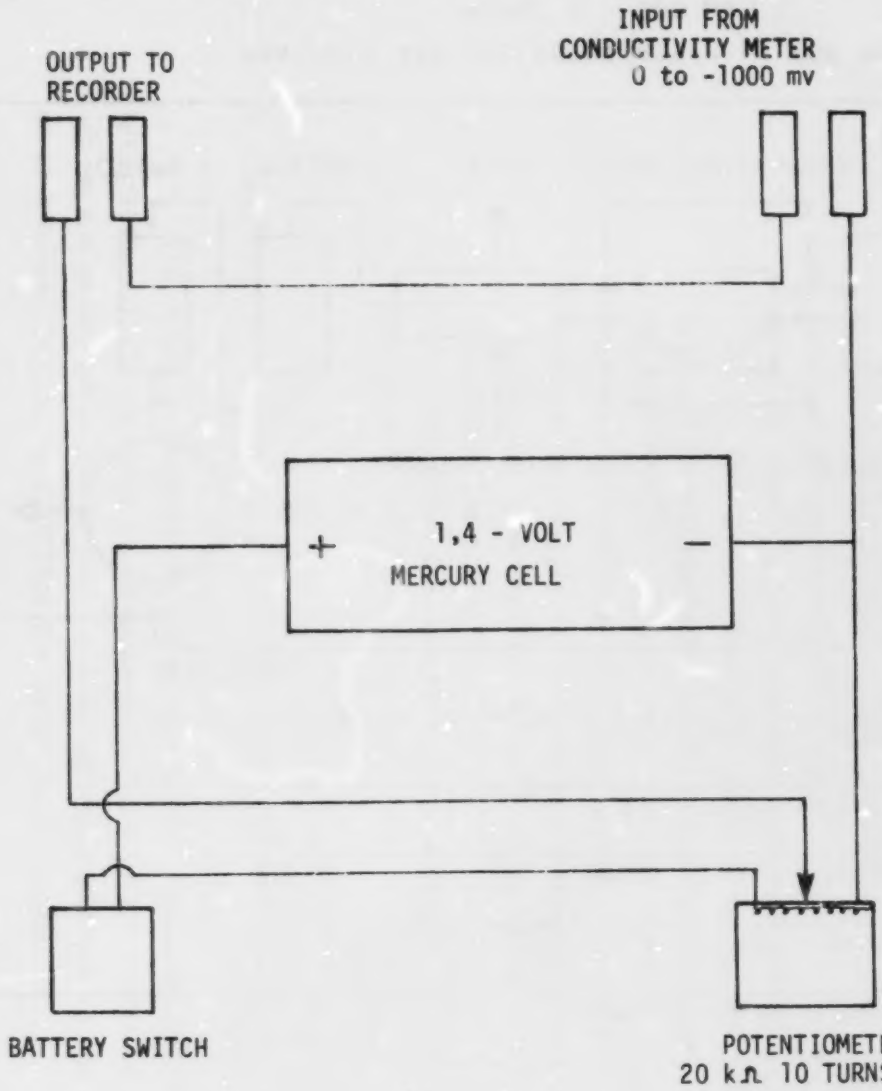
## 8. COLUMNS

The column assemblies are shown in figure 1. We have obtained satisfactory results with 16 x 150 mm pyrex culture tubes, shortened to 125 mm and drawn out at the bottom. A 5-ml syringe connected to the top of each column is used to stabilize the water level inside.




MANIFOLD AND EQUIPMENT ASSEMBLY FOR METHOD I-A
RANGE 0 - 200 µe / l

FIGURE 3




BASELINE OFFSET INTERFACE

FIGURE 4

If one wished to work with lower flow rates, one could use smaller columns and a conductivity cell with a constant of .316 $cm^{-1}$. But under these conditions packing and degassing the columns become more difficult, and flow blockages more common.

The life of a column depends on various factors, including the volume and ionic strength of the samples and the exchange capacity of the resin. In general, a column should be good for 1 000 to 2 000 analyses. The resin may be regarded as still activated if no signal is obtained from a 100-µe/L standard of strong acid and identical signals are obtained from 100-µe/L standards of NaCl, $KNO_3$, $Na_2SO_4$, and $NaHCO_3$.

## 9. PROCEDURE

9.1 With the apparatus assembled as in figure 3 and the 3-way valve open to the drain and not to the columns, start the pump.

9.2 Start the flow of argon to the wash tube.

9.3 When the flow pattern in the coil becomes regular, open the 3-way valve to the columns, adjust the water level in the columns with the syringes, and allow the system to equilibrate for about 20 minutes.

9.4 Set the conductivity meter to the 0-15 µmhos/cm range

9.5 Set the recorder to 50 mV/cm and 1 cm/min and zero it using the interface unit.

9.6 Insert the 15-mL tubes containing the samples and standards into the sample tray; and 100 µL of 0.01 N nitric acid to each tube; set the sample rate to 20/h with a 2:1 sample-to-wash ratio; adjust the recorder response

to full scale for the 200-µe/L standard.

Note that a tube of demineralized water must be positioned before the first standard on the sample tray, so that this standard can be bubbled with the argon. Glass tubes should not be used for the samples. We recommend 16 x 100 mm or 16 x 125 mm polystyrene tubes, with the adapters required for the sample tray.

## 10. CALCULATIONS

See section II.

## 11. INTERFERENCES

See section V.

I-B

# DETERMINATION OF TOTAL ION CONCENTRATION

# LESS

# CONCENTRATION OF ALKALINE IONS

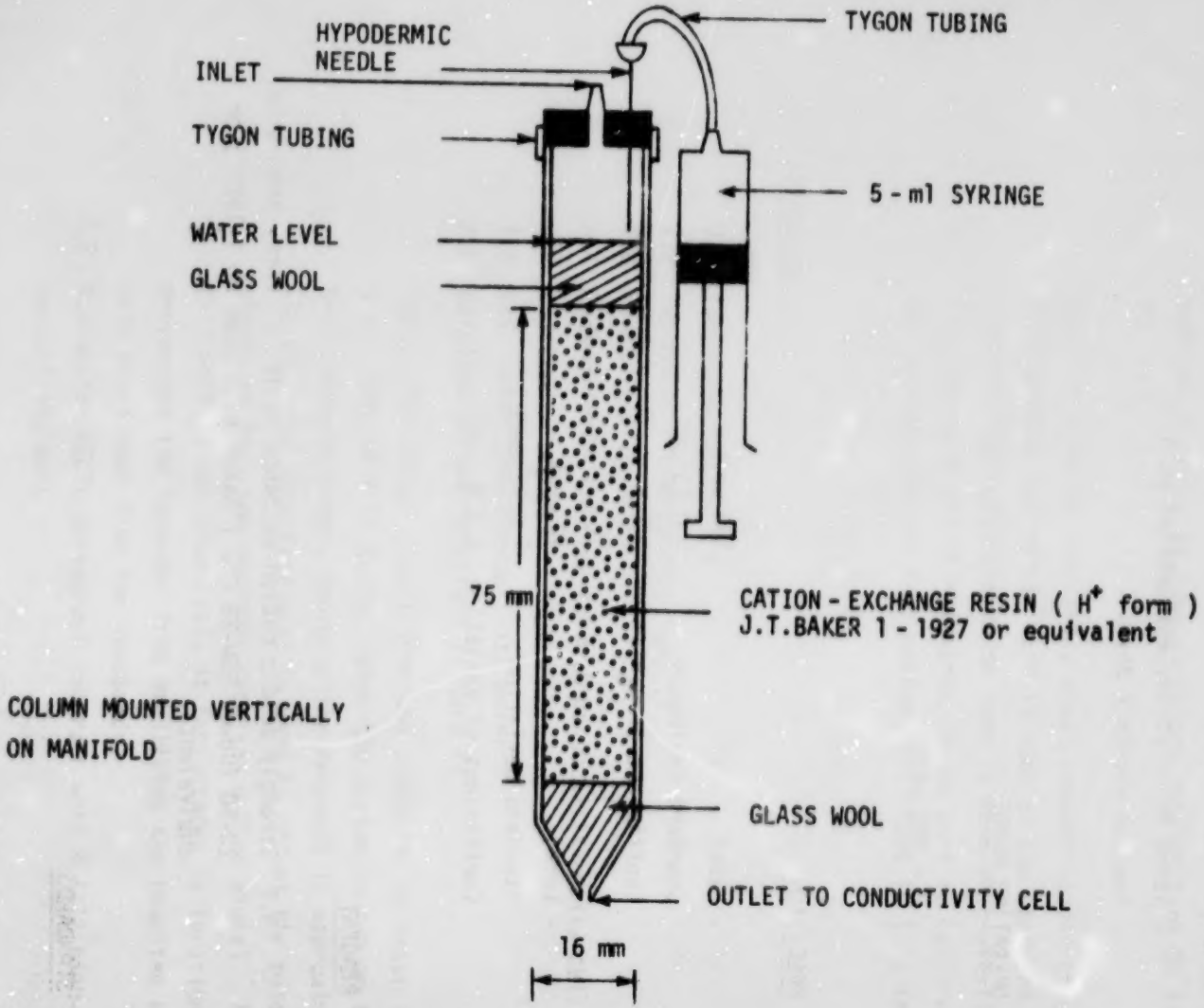
# ($OH^-$, $CO_3^{--}$, $HCO_3^-$)

## 1. PRINCIPLE

The sample is aspirated into the system, diluted 1:4 with demineralized water, and then passed into the ion-exchange column (figure 5), which has been packed with a strongly acidic cation-exchange resin ($H^+$ form). The salts present in the sample are converted into acids such as $H_2SO_4$, HCl, $HNO_3$, $H_3PO_4$, HF, and $H_2CO_3$. These acids are all strong electrolytes, except for $H_2CO_3$ (carbonic acid), which remains undissociated in water.

The concentration of dissociated hydrogen ions in the effluent from the column is equivalent to the total ion concentration of the sample, less the concentration of alkaline ions. This hydrogen-ion concentration of the effluent can be quantified by measurement of its electrical conductivity. Because the equivalent conductances of sulfuric, hydrochloric, and nitric acids are nearly identical (429, 426, and 421 µmhos/cm at $25^{o}$ C), the conductivity of the effluent will be proportional to the ion concentration. In order to minimize interionic effects, which are different for mono-monovalent and mono-divalent salts, the system should be operated with relatively low concentrations (concentration of the column effluent should be of the order of $5 \times 10^{-5}$ N). In this way, a linear response can be obtained from the system.

Because conductivity varies approximately 2 % per degree Celsius, the liquid in the conductivity cell must be kept at constant temperature. The laboratory should therefore prepare sufficient dilution water for a full day's operation far enough in advance for it to come up to room temperature. Given the additional time the sample spends in the system before reaching the cell, a temperature-stabilizing bath for the cell should then not be essential.




ION - EXCHANGE COLUMN FOR METHOD I - B

FIGURE 5

## 2. STORAGE OF SAMPLES

- Store in polypropylene bottles at $5^{o}$ C.
- Analyse within 7 days.

## 3. OPERATING RANGE

- 2 - 200 µe/L

## 4. PRECISION

| | |
|---|---|
| - Level | 100 µe/L |
| Standard deviation | $\pm$ 0.13 µe/L |
| Coefficient of variation | 0.1 % |
| - Level | 40 µe/L |
| Standard deviation | $\pm$ 0.11 µe/L |
| Coefficient of variation | 0.3 % |

## 5. REAGENT

5.1 Strongly acidic cation-exchange resin, $H^{+}$ form, mesh size 20-50 (Dowex 50W-X8 [ J T Baker catalogue No 1-1927 ] or equivalent)

## 6. STANDARDS

6.1 1.0 N ammonium sulfate

6.2 1.0 N nitric acid

6.3 Prepare an intermediate solution containing 10 000 µe/L nitric acid and 10 000 µe/L ammonium sulfate

6.4 Prepare a set of standard solutions containing this intermediate solution in concentrations ranging from 20 to 200 µe/L

Note: A solution containing equal concentrations of ammonium sulfate and nitric acid is used as the standard in order to replicate the major ions in acid precipitation. Thus the same set of standards can be used to calibrate the systems for all four methods described in this text.

## 7. APPARATUS

7.1 Tehcnicon Sampler IV

7.2 Technicon Proportioning Pump III

7.3 Manifold (figure 6)

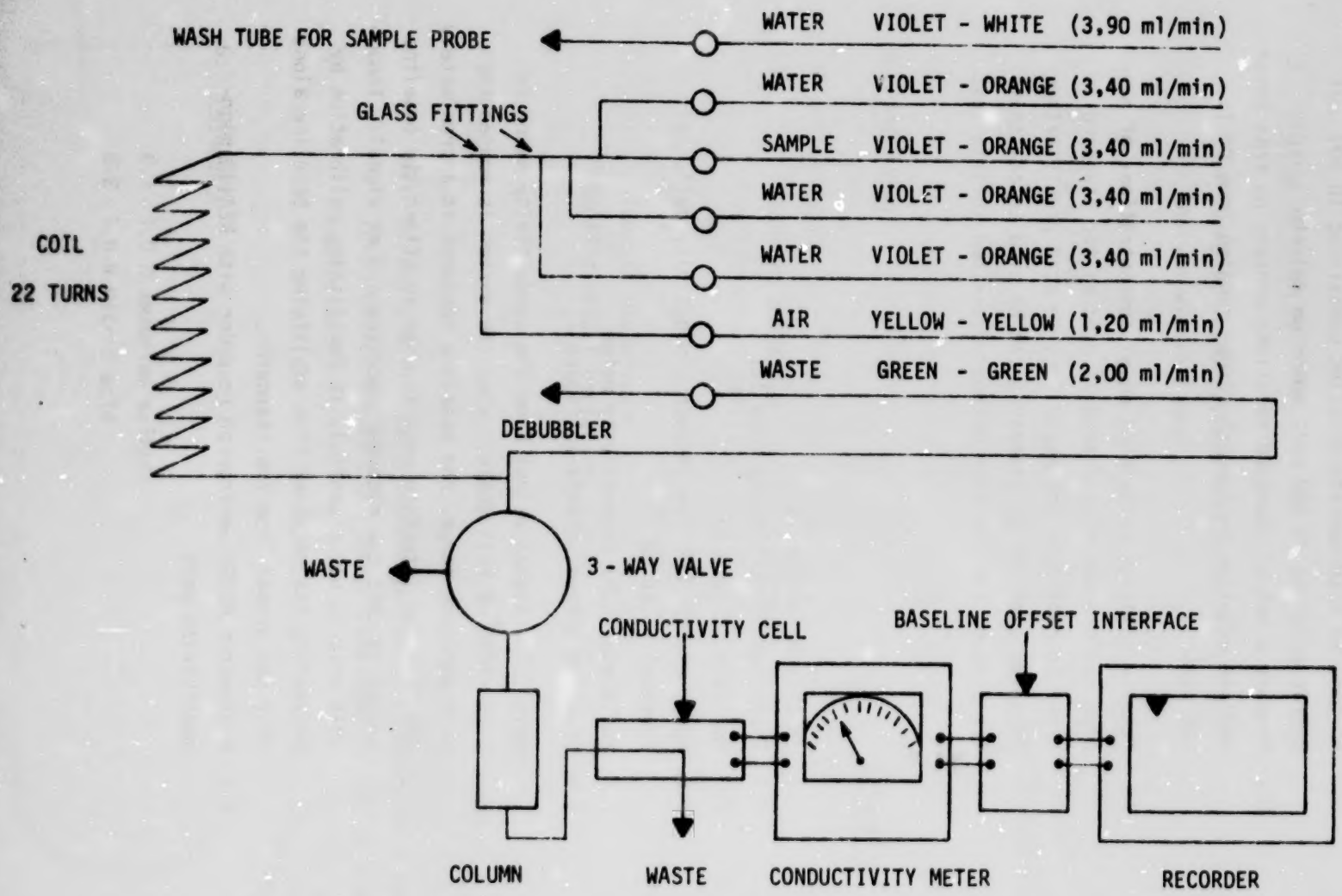
7.4 Radiometer CDC114 flow-through conductivity cell, cell constant = .66 $cm^{-1}$

7.5 Radiometer CDM3 conductivity meter

7.6 Baseline offset interface (figure 7)

Note: The signal output from the conductivity meter is 0 to -1000 mV full scale. When the system is run on the 0-15 µmhos/cm range, the baseline response is approximately -75 mV. The interface unit is used to offset the baseline signal so that the recorder receives a 0 mV signal. Though this unit is not essential, it facilitates calibration by preventing the recorder from amplifying the baseline along with the signal from the standards.

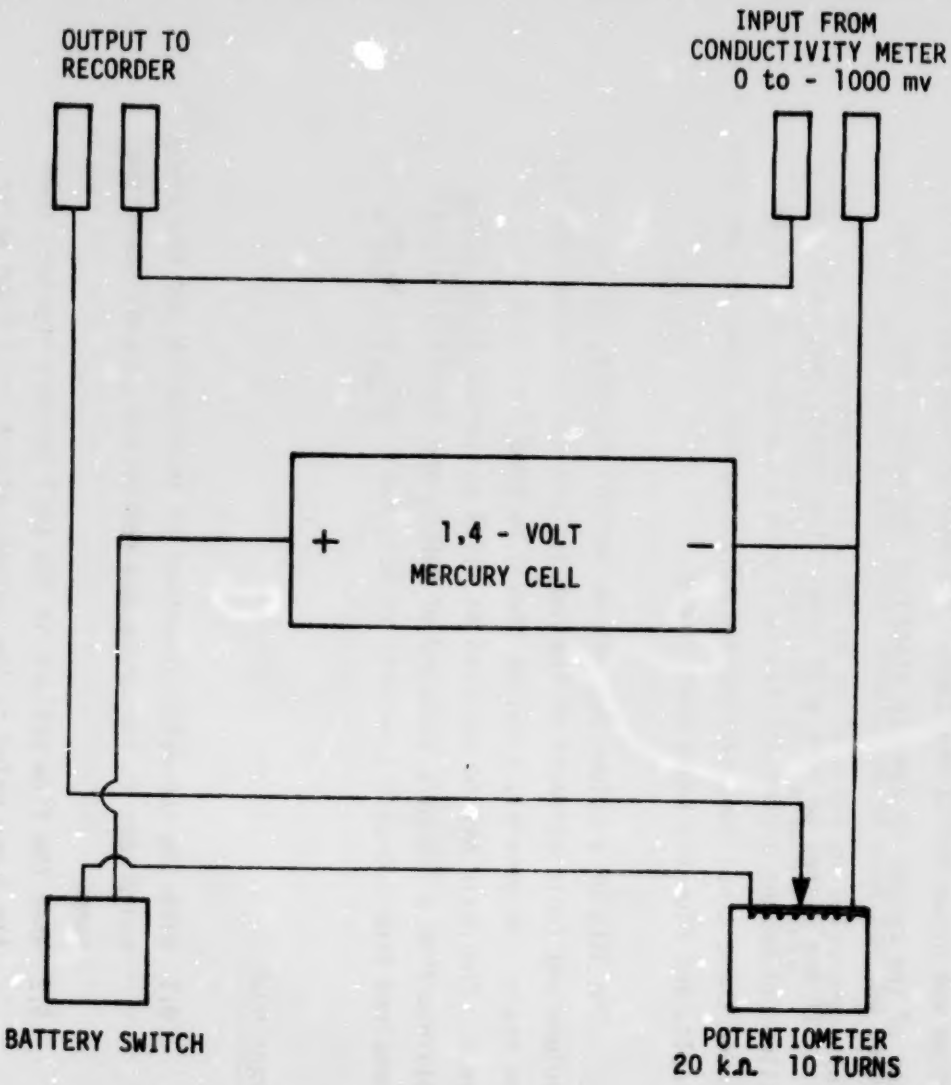
7.7 Radiometer REC80 Servograph recorder with REA112 high-sensitivity unit




MANIFOLD AND EQUIPMENT ASSEMBLY FOR METHOD I-B

RANGE 0 - 200 µe / l

FIGURE 6




BASELINE OFFSET INTERFACE

FIGURE 7

## 8. COLUMN

The column assembly is shown in figure 5. We have obtained satisfactory results with a 16 x 150 mm pyrex culture tube, shortened to 125 mm and drawn out at the bottom. A 5-ml syringe connected to the top of the column is used to stabilize the water level inside.

If one wished to work with lower flow rates, one could use a smaller column and a conductivity cell with a constant of .316 $cm^{-1}$. But under these conditions packing and degassing the column become more difficult, and flow blockages more common.

The life of a column depends on various factors, including the volume and ionic strength of the samples and the exchange capacity of the resin. In general, a column should be good for 1 000 to 2 000 analyses. The resin may be regarded as still activated if no signal is obtained from a 100-µe/L standard of $NaHCO_3$ and identical signals are obtained from 100-µe/L standards of HCl, NaCl, $KNO_3$, and $Na_2SO_4$.

## 9. PROCEDURE

9.1 With the apparatus assembled as in figure 6 and the 3-way valve open to the drain and not to the column, start the pump.

9.2 When the flow pattern in the coil becomes regular, open the 3-way valve to the column, adjust the column water level with the syringe, and allow the system to equilibrate for about 20 minutes.

9.3 Set the conductivity meter to the 0-15 µmhos/cm range.

9.4 Set the recorder to 50 mV/cm and 1 cm/min and zero it using the interface unit.

9.5 Insert the tubes containing the samples and standards into the sample tray; set the sample rate to 20/h with a 2:1 sample-to-wash ratio; adjust the recorder response to full scale for the 200-µe/L standard.

Note that glass tubes should not be used for the samples. we recommend 16 x 100 mm or 16 x 125 mm polystyrene tubes, with the adapters required for the sample tray.

## 10. CALCULATIONS

See section II.

## 11. INTERFERENCES

See section V.

I-C

# DETERMINATION OF TOTAL ION CONCENTRATION

# LESS

# CONCENTRATION OF ALKALINE IONS ($OH^-$, $CO_3^{--}$, $HCO_3^-$)

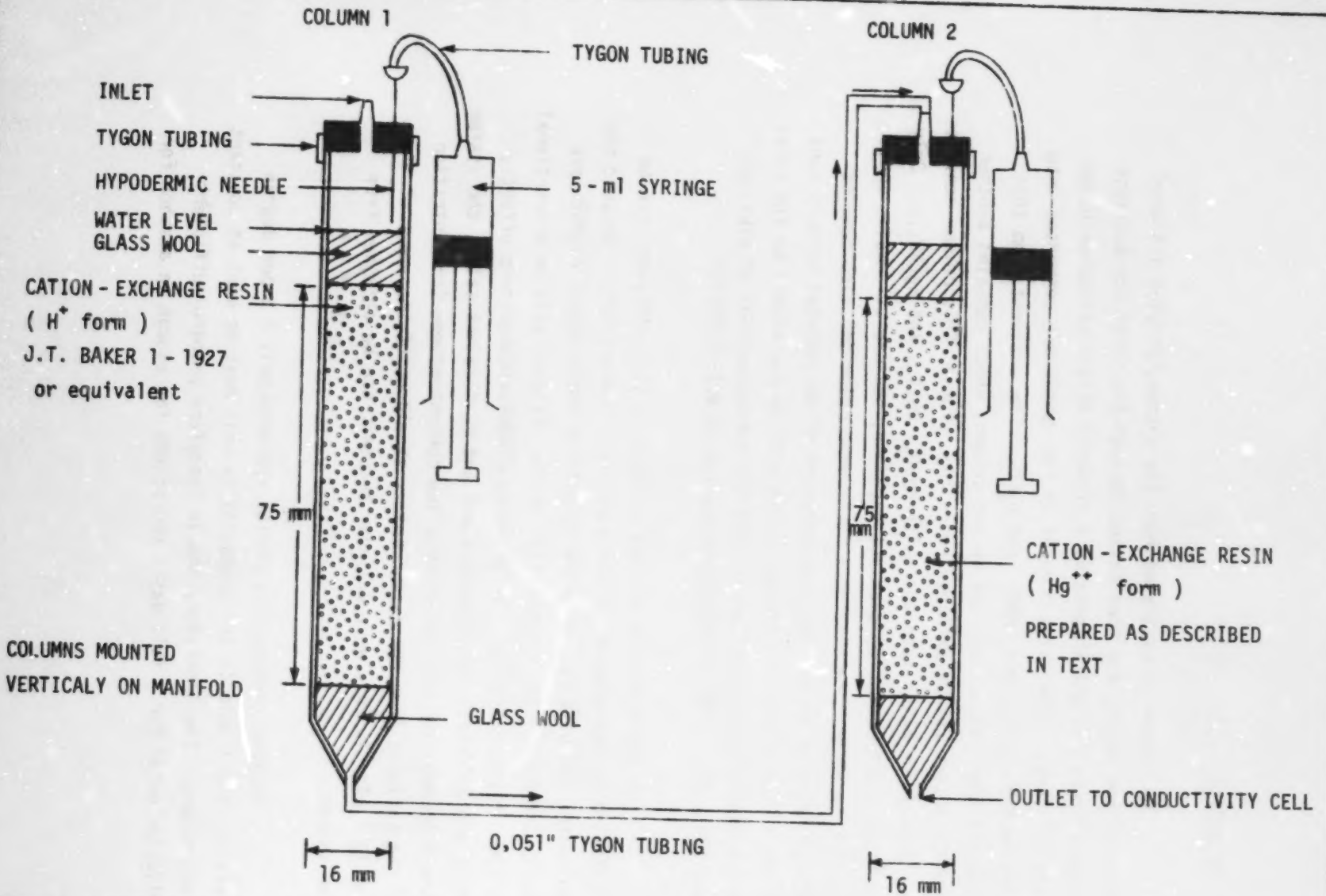
# AND CHLORIDE IONS ($Cl^-$)

## 1. PRINCIPLE

The sample is aspirated into the system, diluted 1:4 with demineralized water, and then passed through the first ion-exchange column (figure 8), which contains a strongly acidic cation-exchange resin ($H^+$ form). The salts present in the sample are converted into acids such as $H_2SO_4$, HCl, $HNO_3$, and $H_2CO_3$. The effluent from this column is then passed into the second column, which contains another strongly acidic cation-exchange resin ($Hg^{++}$ form). This column converts the first three acids into the salts $HgSO_4$, $HgCl_2$, and $Hg(NO_3)2$. Only the $H_2CO_3$ (carbonic acid) does not exchange, because it remains undissociated in water. Bacause $HgCl_2$ (mercuric chloride) also remains undissociated in water, the concentration of dossociated mercury ions in the effluent from the second column will be equivalent to the total ion concentration of the sample less the concentrations of alkaline ions ($OH^-$, $CO_3^{--}$, $HCO_3^-$) and chloride ions ($Cl^-$).

The concentration of mercury ions in this effluents can be quantified by measurement of its electrical conductivity. Because the equivalent conductances of mercuric sulfate and mercuric nitrate are nearly identical, the conductivity of the effluent will be proportional to the ion concentration. In order to minimize interionic effects, which are different for di-monovalent and di-divalent salts, the system should be operated with relatively low concentrations (concentration of the effluent from the second column should be of the order of $5 \times 10^{-5}$ N). In this way, a linear response can be obtained from the system.

Because conductivity varies approximately 2 % per degree Celsius, the liquid in the conductivity cell must be kept at constant temperature. The laboratory should therefore prepare sufficient dilution water for a full day's operations far enough in advance for




ION - EXCHANGE COLUMNS FOR METHOD I - C

FIGURE 8

it to come up to room temperature. Given the additional time the sample spends in the system before reaching the cell, a temperature-stabilizing bath for the cell should then not be essential.

## 2. STORAGE OF SAMPLES

- Store in polypropylene bottles at $5^{o}$ C.
- Analyse within 7 days.

## 3. OPERATING RANGE

- 2 - 200 µe/L

## 4. PRECISION

| | |
|---|---|
| - Level | 100 µe/L |
| Standard deviation | ± 0.12 µe/L |
| Coefficient of variation | 0.1 % |
| - Level | 40 µe/L |
| Standard deviation | ± 0.10 µe/L |
| Coefficient of variation | 0.2 % |

## 5. REAGENTS

5.1 Saturated solution $Hg(NO_3)2 \cdot H_2O$
(Dissolve 20 g mercuric nitrate in 2 L water, agitate for 1 h, and filter.)

5.2 Strongly acidic cation-exchange resin, $H^+$ form, mesh size 20-50 (Dowex 50W-X8 [ J T Baker catalogue No 1-1927 ] or equivalent)

5.3 Strongly acidic cation-exchange resin, $Hg^{++}$ form, mesh 20-50 (Prepare this resin by pumping 2 L of the saturated mercuric nitrate solution through a column of cation-exchange resin (in $H^+$ form) at a rate of 3 mL/min. Using a faster rate or a smaller volume of solution may reduce performance. To complete preparation, rinse the column with demineralized water.)

## 6. STANDARDS

6.1 1.0 N ammonium sulfate

6.2 1.0 N nitric acid

6.3 Prepare an intermediate solution containing 10 000 µe/L nitric acid and 10 000 µe/L ammonium sulfate

6.4 Prepare a set of standard solutions containing this intermediate solution in concentrations ranging from 20 to 200 µe/L.

Note: A solution containing equal concentrations of ammonium sulfate and nitric acid is used as the standard in order to replicate the major ions in acid precipitation. Thus the same set of standards can be used to calibrate the systems for all four methods described in this text.

## 7. APPARATUS

7.1 Technicon Sampler IV

7.2 Technicon Proportioning Pump III

7.3 Manifold (figure 9)

7.4 Radiometer CDC114 flow-through conductivity cell, cell constant = .66 $cm^{-1}$

7.5 Radiometer CDM3 conductivity meter

7.6 Baseline offset interface (figure 10)

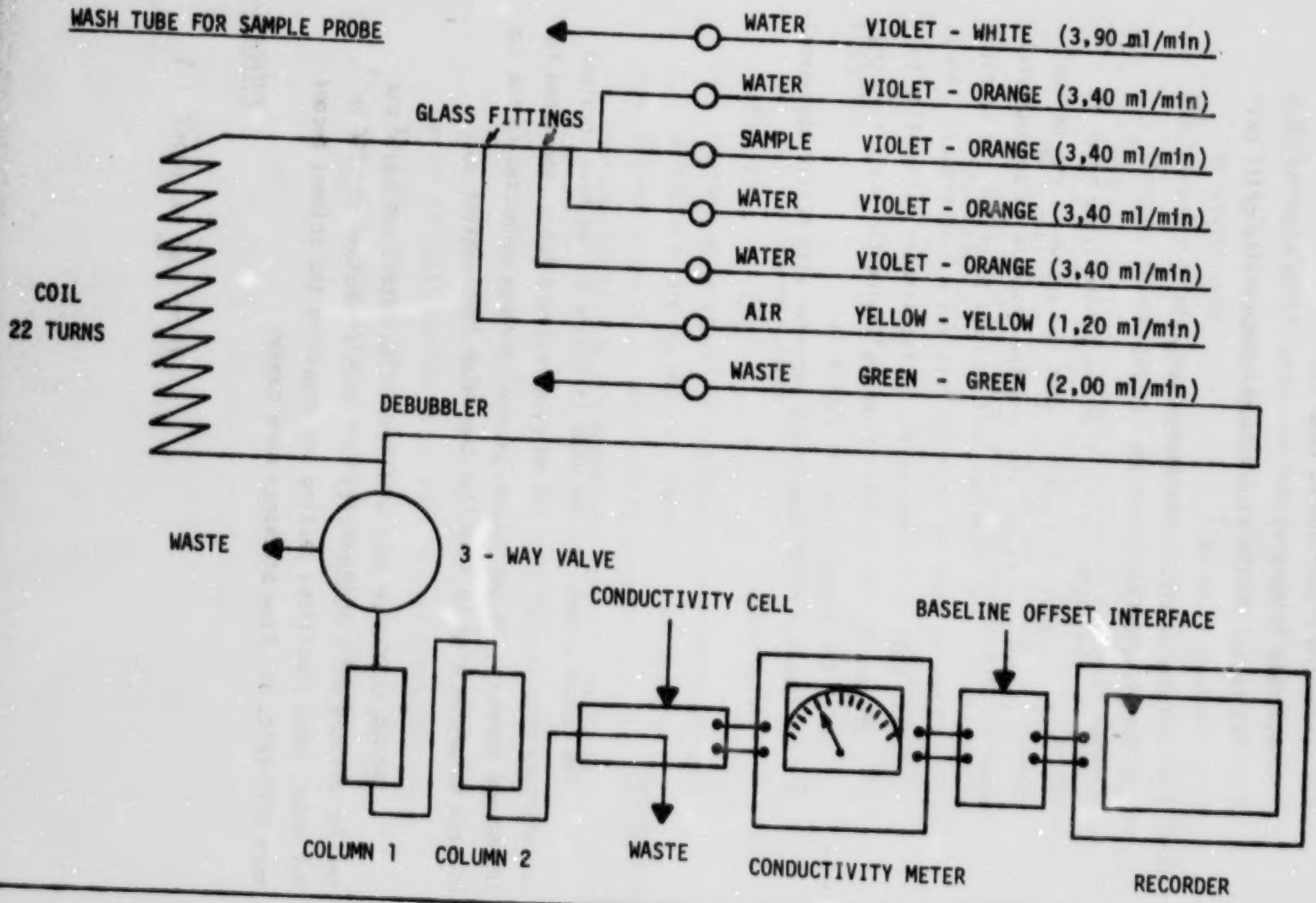
Note: The signal output from the conductivity meter is 0 to -1000 mV full scale. When the system is run on the 0-15 µmhos/cm range, the baseline response is approximately -100 mV. The interface unit is used to offset the baseline signal so that the recorder receives a 0 mV signal. Though this unit is not essential, it facilitates calibration by preventing the recorder from amplifying the baseline along with the signal from the standards.

7.7 Radiometer REC80 Servograph recorder with REA112 high-sensitivity unit.

## 8. COLUMNS

The column assemblies are show in figure 8. We have obtained satisfactory results with 16 x 150 mm pyrex culture tubes, shortened to 125 mm and drawn out at the bottom. A 5-ml syringe connected to the top of each column is used to stabilize the water level inside.

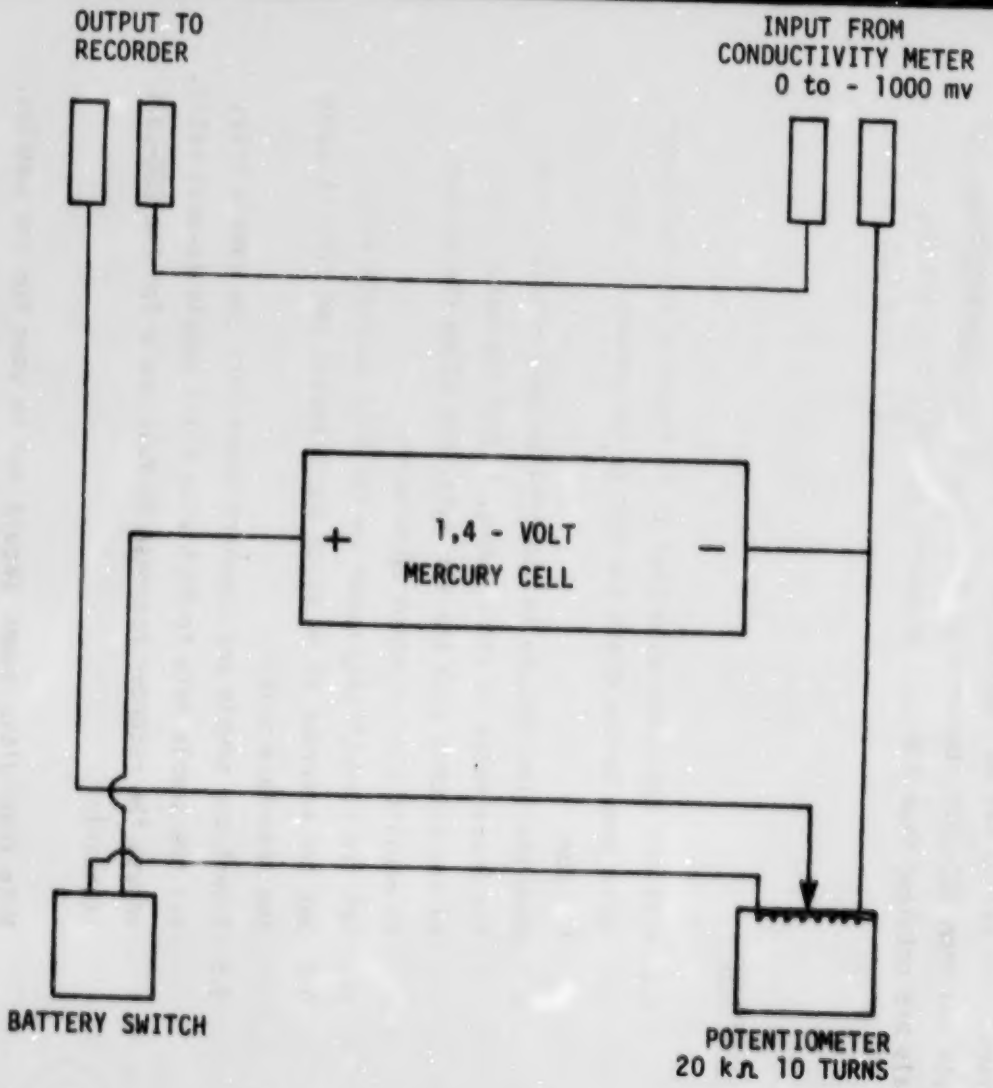
If one wished to work with lower flow rates, one could use smaller columns and a conductivity cell with a constant of .316 $cm^{-1}$. But under these conditions packing and degassing the columns become more difficult, and flow blockages more common.




MANIFOLD AND EQUIPMENT ASSEMBLY FOR METHOD I-C

RANGE 0 - 200 µg/ml

FIGURE 9




BASELINE OFFSET INTERFACE

FIGURE 10

The life of a column depends on various factors, including the volume and ionic strength of the samples and the exchange capacity of the resin. In general, a column should be good for 1 000 to 2 000 analyses. The resins may be regarded as still activated if no signal is obtained from 100-µe/L standards of $NaHCO_3$ and NaCl and identical signals are obtained from 100-µe/L standards of $HNO_3$, $KNO_3$ and $Na_2SO_4$.

## 9. PROCEDURE

9.1 With the apparatus assembled as in figure 9 and the 3-way valve open to the drain and not to the columns, start the pump.

9.2 When the flow pattern in the coil becomes regular, open the 3-way valve to the columns, adjust the water level in the columns with the syringes, and allow the system to equilibrate for about 20 minutes.

9.3 Set the conductivity meter to the 0-15 µmhos/cm range.

9.4 Set the recorder to 50 mV/cm and 1 cm/min and zero it using the interface unit.

9.5 Insert the sample and standard tubes into the sample tray; set the sample rate to 20/h with a 2:1 sample-to-wash ratio; adjust the recorder response to full scale for the 200-µe/L standard.

Note that glass tubes should not be used for the samples. We recommend 16 x 100 mm or 16 x 125 mm polystyrene tubes, with the adapters required for the sample tray.

## 10. CALCULATIONS

See section II.

## 11. INTERFERENCES

See section V.

I-D

# DETERMINATION OF TOTAL ION CONCENTRATION

# LESS

# CONCENTRATION OF ALKALINE IONS ($OH^-$, $CO_3^{--}$, $HCO_3^-$)

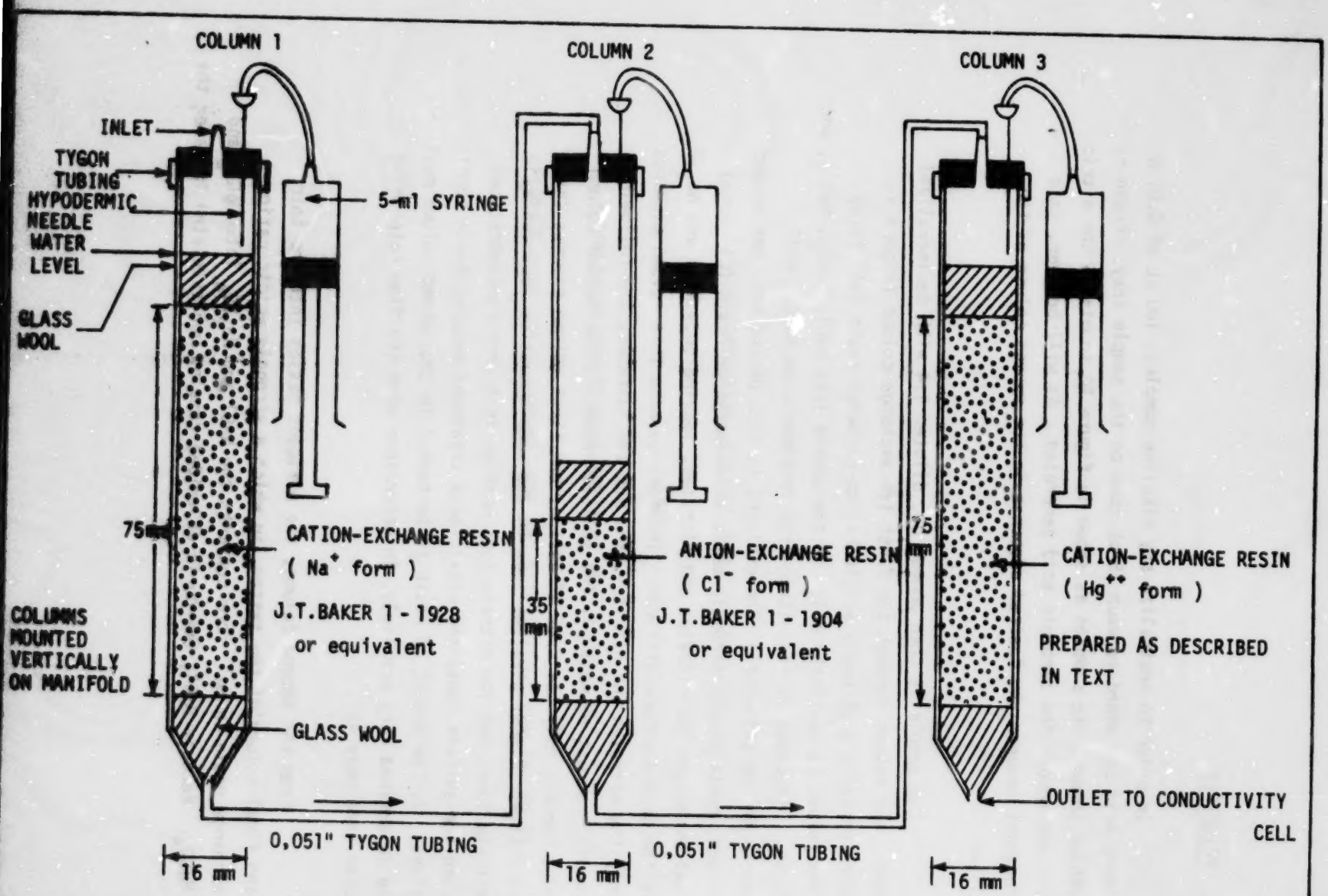
# CHLORIDE IONS ($Cl^-$), AND NITRATE AND NITRITE IONS ($NO_3^- + NO_2^-$)

## 1. PRINCIPLE

In order to neutralize any alkaline samples, 100 µL of 0.01 N nitric acid are added to each 15-mL tube on the sample tray. Argon is bubbled through the samples as shown in figure 12, to mix in the nitric acid and remove the carbonic acid generated. As will be seen, this treatment ensures the desired response in the second column of the system.

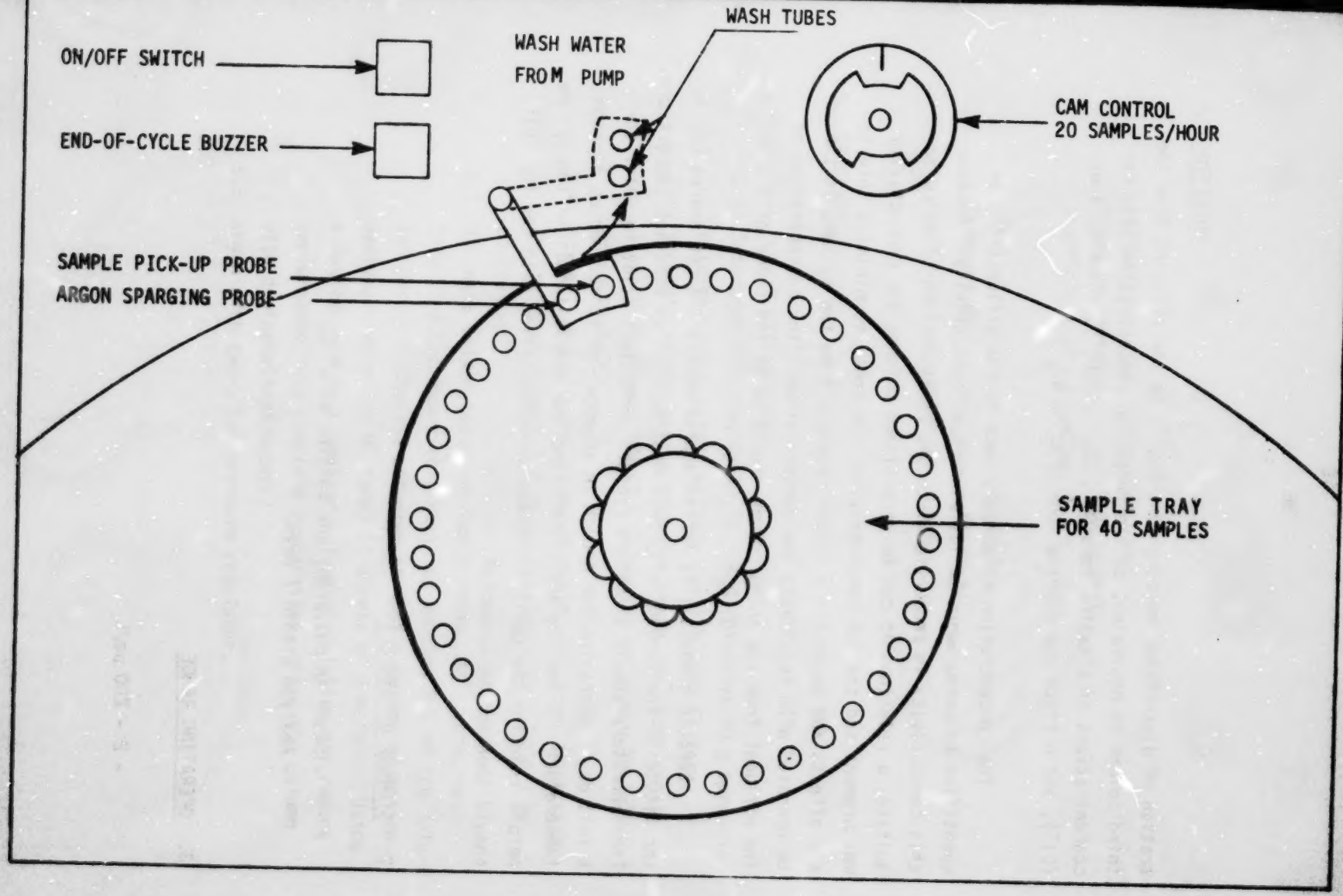
The sample is then pumped up, diluted 1:4 with demineralized water, and passed through the first ion-exchange column (figure 11), which contains a strongly acidic cation-exchange resin ($Na^+$ form). This column converts the salts in the sample into NaCl, $NaNO_2$, $NaNO_3$, and $Na_2SO_4$. (Because of the nitric-acid treatment, no $NaHCO_3$ will appear in the effluent.) The effluent is then passed into the second column, containing a strongly basic anion-exchange resin ($Cl^-$ form) that exchanges the nitrates and nitrites, leaving only NaCl and $Na_2SO_4$ in the second-column effluent. In order to make this column exchange only the nitrates and nitrites, and not the sulfates, the following conditions must be met: 1. The solution entering the second column must contain only one type of cation; the first column ensures this condition; 2. Any alkaline ions in the sample must be replaced by nitrate ions, and the nitrate ions must be in higher concentrations than the sulfate ions; the nitric-acid treatment ensures these conditions; 3. The amount of resin to be packed in the second column must be determined very precisely, in accordance with the flow rate being used (see page 42).

From the second column, the effluent passes into the third and final column of the system, in which a strongly acidic cation-exchange resin in $Hg^{++}$ form converts the NaCl and $Na_2SO_4$ into $HgCl_2$ and $HgSO_4$. Because $HgCl_2$ (mercuric chloride) remains undissociated in water, the




ION - EXCHANGE COLUMNS FOR METHOD I - D

FIGURE 11




SAMPLER - TOP VIEW

FIGURE 12

tration of dissociated mercury ions ($Hg^{++}$) in the effluent from the third column in equivalent to the total ion concentration less the concentrations of alkaline ions($OH^-$, $CO_3^{--}$, $HCO_3^-$), chloride ions ($Cl^-$), and nitrate and nitrite ions ($NO_3^-$ + $NO_2^-$).

The concentration of mercury ions in the effluent can be quantified by measurement of its electrical conductivity. Because this conductivity is proportional to the concentration of mercuric sulfate, a relationship can be established between the conductivity measurement and the ion concentration. In order to minimize interionic effects and so obtain a linear response from the system, it should be operated with relatively low concentrations (ion concentration of the effluent from the third column should be of the order of $5 \times 10^{-5}$ N).

Because conductivity varies approximately 2 % per degree Celsius, the liquid in the conductivity cell must be kept at constant temperature. The laboratory should therefore prepare sufficient dilution water for a full day's operation far enough in advance for it to come up to room temperature. Given the additional time the sample spends in the system before reaching the cell, a temperature-stabilizing bath for the cell should then not be essential.

## 2. STORAGE OF SAMPLES

- Store in polypropylene bottles at $5^{o}$ C.
- Analyse within 7 days.

## 3. OPERATING RANGE

- 2 - 200 µe/L

## 4. PRECISION

| | |
|---|---|
| - Level | 100 µe/L |
| Standard deviation | ± 0.39 µe/L |
| Coefficient of variation | 0.4 % |
| - Level | 40 µe/L |
| Standard deviation | ± 0.24 µe/L |
| Coefficient of variation | 0.6 % |

## 5. REAGENTS

5.1 0.01 N nitric acid

5.2 Saturated solution $Hg(NO_3)2 \cdot H_2O$ (Dissolve 20 g mercuric nitrate in 2 L water, agitate for 1 h, and filter.)

5.3 Strongly acidic cation-exchange resin, $Na^+$ form, mesh size 20-50 (Dowex 50W-X8 [ J T Baker catalogue No 1-1928 ] or equivalent)

5.4 Strongly basic anion-exchange resin, $Cl^-$ form, mesh size 20-50 (Dowex 1-X8 [ J T Baker catalogue No 1-1904 ] or equivalent)

5.5 Strongly acidic cation-exchange resin, $Hg^{++}$ form, mesh size 20-50 (Prepare this resin by pumping 2 L of the satuted mercuric nitrate solution through a column of cation-exchange resin (in $H^+$ form) at a rate of 3 mL/min. Using a faster rate or a smaller volume of solution may reduce performance. To complete preparation, rinse the column with demineralized water.)

5.6 Argon with two-stage pressure regulator.

## 6. STANDARDS

6.1 1.0 N ammonium sulfate

6.2 1.0 N nitric acid

6.3 Prepare an intermediate solution containing 10 000 μe/L nitric acid and 10 000 μe/L ammonium sulfate

6.4 Prepare a set of standard solutions containing this intermediate solution in concentrations ranging from 40 to 400 μe/L.

Note: A solution containing equal concentrations of ammonium sulfate and nitric acid is used as the standard in order to replicate the major ions in acid precipitation. Thus the same set of standards can be used to calibrate the systems for all four methods described in this text.

Though 40 to 400 μe/L is the actual range of total ion concentrations of the standards, their effective calibration range in method I-D will be 20 to 200 μe/L, because this method determines total ion concentration less the concentration of alkaline, chloride, nitrate, and nitrite ions.

## 7. APPARATUS

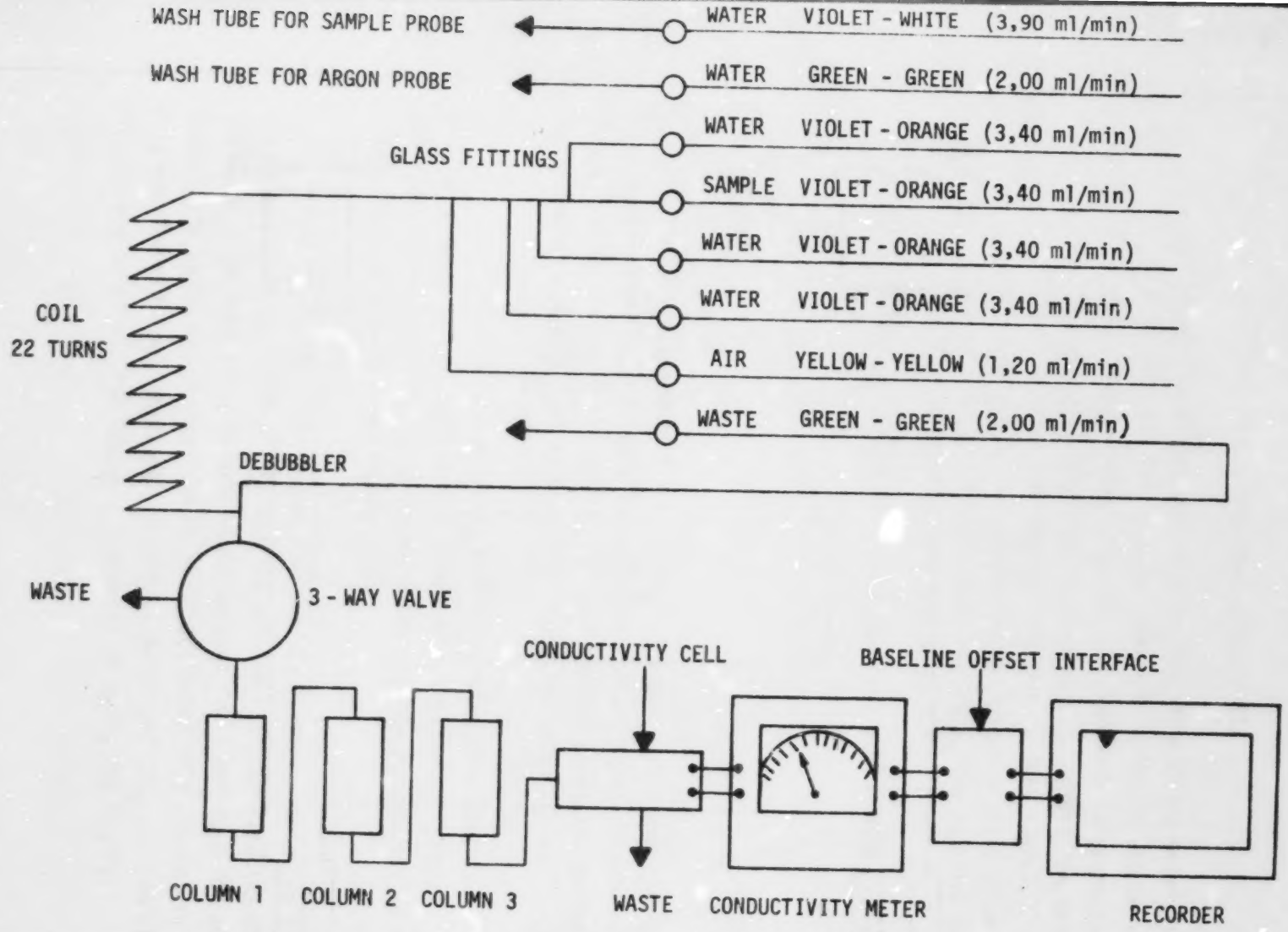
7.1 Technicon Sampler IV (Figure 12)

7.2 Technicon Proportioning Pump III

7.3 Manifold (figure 13)

7.4 Radiometer CD114 flow-through conductivity cell, cell constant = .66 $cm^{-1}$

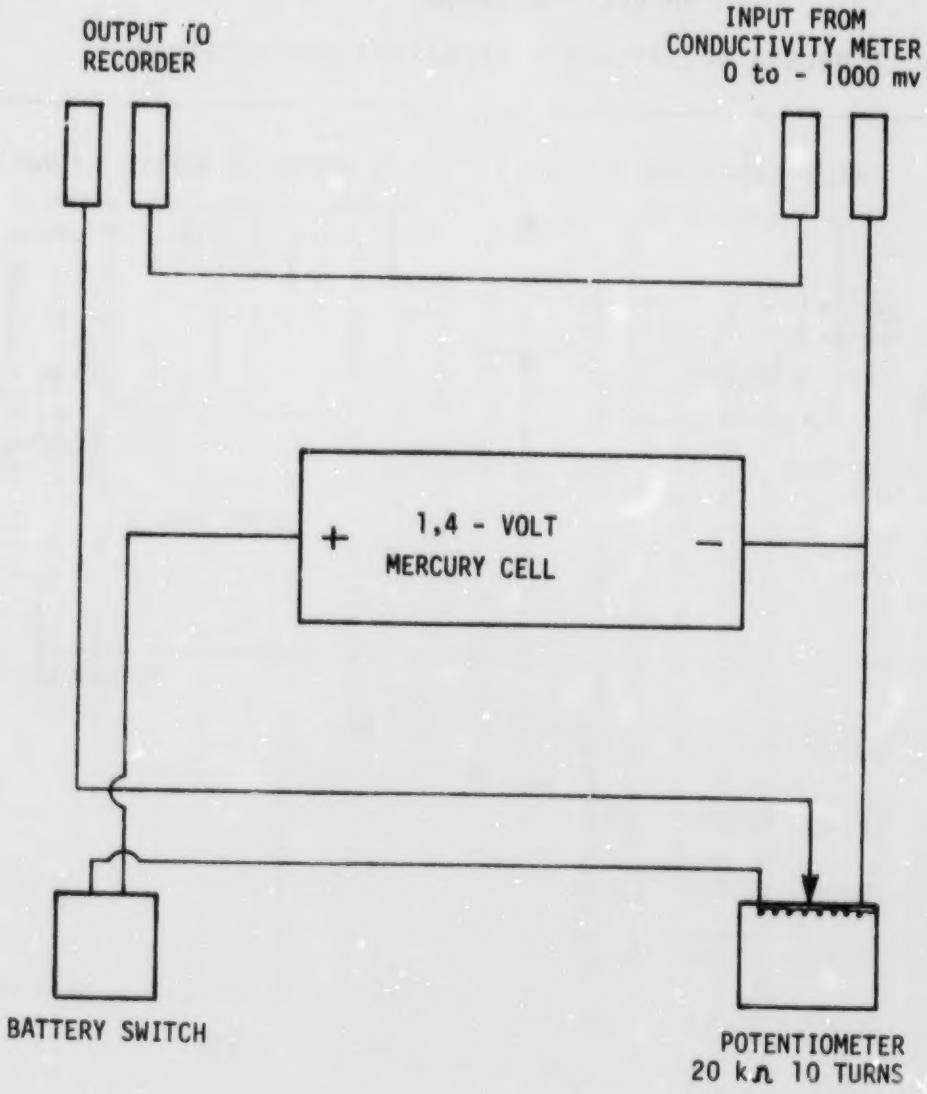
7.5 Radiometer CDM3 conductivity meter




MANIFOLD AND EQUIPMENT ASSEMBLY FOR METHOD I - D

RANGE 0 - 200 µe / l

FIGURE 13




BASELINE OFFSET INTERFACE

FIGURE 14

7.6 Baseline offset interface (figure 14)

Note: The signal output from the conductivity meter is 0 to -1000 mV full scale. When the system is run on the 0-15 µmhos/cm range, the baseline response is approximately -250 mV. The interface unit is used to offset the baseline signal so that the recorder receives a 0 mV signal. Though this unit is not essential, it facilitates calibration by preventing the recorder from amplifying the baseline along with the signal from the standards.

7.7 Radiometer REC80 Servograph recorder with REA112 high-sensitivity unit.

## 8. COLUMNS

The column assemblies are shown in figure 11. We have obtained satisfactory results with 16 x 150 mm pyrex culture tubes, shortened to 125 mm and drawn out at the bottom. A 5-ml syringe connected to the top of each column is used to stabilize the water level inside.

If one wished to work with lower flow rates, one could use smaller columns and a conductivity cell with a constant of .316 $cm^{-1}$. But under these conditions packing and degassing the columns become more difficult, and flow blockages more common.

The life of a column depends on various factors, including the volume and ionic strength of the samples and the exchange capacity of the resin. In general, a column should be good for 1 000 to 2 000 analyses. The resin may be regarded as still activated if no signal is obtained from 100-µe/L standards of $NaHCO_3$, NaCl, and $KNO_3$ and identical signals are obtained from 100-µe/L standards of $H_2SO_4$ and $Na_2SO_4$.

The amount of chloride-form anion-exchange resin to be used in the second column is determined as follows. Using a 100-µe/L standard of $KNO_3$, determine how much resin is required for the peak height on the recorder to be less than 1 % of full scale. A 35-mm column of resin will generally provide good results. If the column is too long, it will be more selective for the sulfate ions, and reduce the recorder response for the samples and standards accordingly.

## 9. PROCEDURE

9.1 With the apparatus assembled as in figure 13 and the 3-way valve open to the drain and not to the columns, start the pump.

9.2 Start the flow of argon to the wash tube.

9.3 When the flow pattern in the coil becomes regular, open the 3-way valve to the columns, adjust the water level in the columns with the syringes, and allow the system to equilibrate for about 20 minutes.

9.4 Set the conductivity meter to the 0-15 µmhos/cm range.

9.5 Set the recorder to 50 mV/cm and 1 cm/min and zero it using the interface unit.

9.6 Insert the 15-mL tubes containing the samples and standards into the sample tray; add 100 µL of 0.01 N nitric acid to each tube; set the sample rate to 20/h with a 2:1 sample-to-wash ratio; adjust the recorder response to full scale for the 200-µe/L standard.

Note that a tube of demineralized water must be positioned before the first standard on the sample tray, so that this standard can be bubbled with the argon. Glass tubes should

not be used for the samples. We recommend 16 x 100 mm or 16 x 125 mm polystyrene tubes, with the adapters required for the sample tray.

## 10. CALCULATIONS

See section II.

## 11. INTERFERENCES

See section V.

II

# CALCULATION OF TOTAL ION CONCENTRATION AND CONSTITUENTS OF PRECIPITATION SAMPLES ANALYSED BY METHODS I-A - I-D

## 1. NOTATION

Let:

$X_1$ = Total ion concentration less hydrogen-ion concentration (as determined by method I-A);

$X_2$ = Total ion concentration less concentration of alkaline ions (as determined by method I-B);

$X_3$ = Total ion concentration less concentration of alkaline ions and chloride ions (as determined by method I-C); and

$X_4$ = Total ion concentration less concentration of alkaline, chloride, nitrate and nitrite ions (as determined by method I-D)

## 2. CALCULATIONS

2.1 If $X_1 > X_2$,
then $X_1$ = total ion concentration, in μe/L,
and $X_1 - X_2$ = total alkalinity, in μe/L.

2.2 If $X_2 > X_1$,
then $X_2$ = total ion concentration, in μe/L,
and $X_2 - X_1$ = hydrogen-ion concentration, in μe/L.

2.3 $X_2 - X_3$ = concentration of chloride ions, in μe/L.

2.4 $X_3 - X_4$ = concentration of nitrate and nitrite ions, in μe/L

2.5 $X_4$ = concentration of sulfate ions, in μe/L

## 3. CONVERSION FACTORS

3.1 Total alkalinity: μe/L X 0.05 = mg/L (as $CaCO_3$)

3.2 Concentration of chloride ions: μe/L X 0.0355 = mg/L (as $Cl^-$)

3.3 Concentration of nitrate ions plus nitrite ions: μe/L X 0.014 = mg/L (as N)

3.4 Concentration of sulfate ions: μe/L X 0.048 = mg/L (as $SO_4^{--}$)

## 4. RECOMMENDATIONS ON SYSTEM OPERATION

4.1 If sufficient equipment to construct a two-channel system is available, the analyses by methods I-A and I-D may be run simultaneously, since both require addition of nitric acid to the sample. One proportioning pump and one sampler will then serve for both analyses.

4.2 The equipment assembly for method I-C can be used for method I-B as well. Since the resin in the single column in method I-B is identical to the resin in the first column in method I-C, one need merely insert another conductivity cell between the columns.

4.3 The drain for the conductivity cells must be at the same level as the columns so that the water in the columns is not siphoned off.

4.4 The 5-ml syringes fixed to the top of the colums serve not only to adjust the water level, but also to indicate problems with the columns. If the piston is forced back by pressure build-up in the system, air has accumulated in the resin or particles have built up in the glass wool, slowing the flow

through it. In this case the columns must be degassed and cleaned.

# III

# THREE METHODS FOR DETERMINING pH OF ACID PRECIPITATION

## A. ELECTROMETRIC METHOD

1. Carefully follow the instructions for the pH meter and prepare the electrode as specified by the manufacturer.
2. Set the temperature compensator to the temperature of the samples. Ensure that the standards are at the same temperature.
3. Standardize the meter with a buffer solution having a pH of 4.00 $\pm$ 0.02. If possible. however, it is preferable to calibrate the meter with a strongly acidic solution whose hydrogen-ion concentration is known to within $\pm$ 1 %. But if a buffer solution is used instead, the electrode must be rinsed frequently so as not to contaminate the samples.
4. Both when standardizing the meter and when measuring the samples, agitate the solution for about one minute. Then wait until the meter reading has been stable for about 30 seconds before you record it. It may take 5 to 10 minutes to get a stable reading, depending on the sample.
5. With the above method and a pH meter accurate to within $\pm$ .1 mV, a precision of $\pm$ 0.02 pH units can be expected for measurements of acid precipitation.

## B. CALCULATION METHOD I

pH is defined as the negative logarithm of hydrogen-ion activity, $A_{H^+}$:

$$pH = - \log_{10} A_{H^+} \qquad (1)$$

The hydrogen-ion concentration can be calculated from:

$$[\ H^+\ ] = \frac{A_{H^+}}{\gamma_{H^+}} \qquad (2)$$

where $\gamma_{H^+}$ is the hydrogen-ion activity coefficient.

$\gamma_{H^+}$ is a function of the ionic strength, I. For solutions with an ionic strength less than $10^{-3}$ M (as is typical of precipitation), the simple Debye-Hückel expression for water at $25^{o}$ C is used with equation (2) to generate:

$$[\ H^+\ ] = (10^{-pH})\ \ (10^{0.5\ X\ I^{\frac{1}{2}}}) \qquad (3)$$

which gives:

$$pH = -\log [\ H^+\ ] + 0.5\ X\ I^{\frac{1}{2}}. \qquad (4)$$

If no correction is made for ionic strength in calculating pH from hydrogen-ion concentration, the associated error will vary from 0.001 to 0.015 pH units for ionic strengths in the range of $10^{-5}$ to $10^{-3}$ M. Hence when extreme accuracy is not required, equation (4) may be simplified to:

$$pH = -\log [\ H^+\ ] \qquad (5)$$

Thus the hydrogen-ion concentration determined by the ion-exchange method can be used to calculate the pH of acid precipitation accurately and avoid the arduous work of getting precise measurements with a pH meter.

## C. CALCULATION METHOD 2

For a given sample, let:

$C$ = total ion concentration, in μe/L;

$\Lambda_o$ = limiting equivalent conductance, in μmhos/cm at 25° C;

$COND_o$ = limiting conductance, in μmhos/cm at 25° C; and

$H^+$ = hydrogen-ion concentration, in μe/L;

where:

$$\Lambda_o = \frac{COND_o}{C} \times 1000 \qquad (1)$$

and $CCND_o$ = Σ of the limiting conductances of all ions in the sample. (2)

As the ratio of bicarbonate ions to total ions in a sample decreases from 1 to 0, the value of $\Lambda_o$ rises from 100 to 140, because $HCO_3^-$ has a low equivalent conductance (44.48) compared with $Cl^-$(76.34), $SO_4^{--}$ (79.8), and $NO_3^-$ (71.44). In contrast, as the ratio of hydrogen ions to total ions increases from 0 to 1, $\Lambda_o$ increases much more markedly, from 140 to 427, because $H^+$ has a much higher equivalent conductance than $Na^+$, $K^+$, $Ca^{++}$, $Mg^{++}$, and $NH_4^+$(349.82, compared with 50.11, 73.52, 59.50, 53.06, and 73.4, respectively). We can therefore write:

$$\frac{\Lambda_o - 140}{\frac{H^+}{C}} = 287 \qquad (3)$$

and developing obtain:

$$\Lambda_o C - 140\,C = 287\,H^+ \qquad (4)$$

and:

$$H^+ = \left[\frac{COND_o - 0.14\,C}{0.287}\right] \qquad (5)$$

The pH of the sample may then be calculated as follows:

$$pH = -\log_{10} \left[ \left( \frac{COND_o - 0.14\ C}{.287} \right) \times 10^{-6} \right] \qquad (6)$$

But if:

$$(COND_o - 0.14C) < 0 \qquad (7)$$

then the sample is alkaline, and its pH will be greater than 5.7.

## D. COMPARISON OF THREE METHODS

Table 1 shows the results of a comparative study of the three pH-determination methods described in the preceding pages.

TABLE 1

| Laboratory # | measured pH | calculated pH (method 1) | calculated pH (method 2) |
|---|---|---|---|
| 47236 | 4.45 | 4.47 | 4.46 |
| 49038 | 4.21 | 4.21 | 4.20 |
| 49108 | 4.18 | 4.17 | 4.16 |
| 49312 | 4.21 | 4.21 | 4.21 |
| 49313 | 4.43 | 4.47 | 4.45 |
| 50357 | 3.78 | 3.79 | 3.79 |
| 53636 | 4.48 | 4.48 | 4.47 |
| 54015 | 4.46 | 4.47 | 4.47 |
| 54016 | 4.29 | 4.30 | 4.30 |
| 54017 | 4.31 | 4.32 | 4.32 |

As can be seen, the results for all three methods are very similar.

We have chosen calculation method 1 for our work with acid precipitation, because method 2 is a new approach and will require further, extensive comparisons.

For alkaline precipitation, neither of the calculation methods is applicable, and pH should be determined by the electrometric method.

# IV

# STORAGE REQUIREMENTS FOR ACID-PRECIPITATION SAMPLES

## 1. INTRODUCTION

To determine storage requirements for acid-precipitation samples, we have conducted a two-month experiment on the stability of the ions usually analysed in them.

## 2. EXPERIMENTAL METHOD

To collect a sufficient sample for this experiment, we installed a Sangamo automatic precipitation collector on the roof of the scientific complex in Ste-Foy, Quebec. Precipitation was collected for three days, 20 to 22 September 1981. The sample was then transferred into two 1-L polypropylene bottles that had never been used and had been rinsed out with demineralized water. Precipitation from both containers was analysed the same day, using the methods described in section I of this text. One container was then stored at $5^{o}$ C, and the other on a table in the laboratory. Additional sets of analyses, using the same methods, were performed on precipitation from both containers on the 16th, 33rd, and 63rd days after we had started collecting the sample.

## 3. RESULTS

Tables 1 and 2 compare the results of the analyses for the sample stored at $5^{o}$ C and the sample stored at room temperature ($22^{o}$ C) in the laboratory.

Table 1 Sample stored at 5° C

| Parameter | Unit | Std deviation | Days after start of sampling 3 | 16 | 33 | 63 |
|---|---|---|---|---|---|---|
| Total ion concentration | µe/L | ± 2 | 90. | 84. | 90. | 93. |
| Conductivity | µmhos/cm | ± 0.2 | 31.2 | 28.2 | 30.5 | 34.5 |
| Hydrogen | µe/L | ± 2 | 68. | 60. | 62. | 67. |
| Sulfate | µe/L | ± 2 | 62. | 58. | 62. | 58. |
| Ammonium | µe/L | ± 1.4 | 18.6 | 20. | 18.6 | 19.3 |
| Nitrate | µe/L | ± 2 | 19. | 19. | 23. | 34. |
| Chloride | µe/L | ± 2 | 5. | 4. | 6. | < 2. |
| Calcium | µe/L | ± 0.5 | 5. | 5.5 | 5.5 | 5. |
| Magnesium | µe/L | ± 0.8 | 0.8 | 0.8 | 0.8 | 0.8 |
| Sodium | µe/L | ± 0.4 | 0.4 | 0.9 | 0.9 | 0.4 |
| Potassium | µe/L | ± 0.3 | 0.8 | 0.8 | 1.0 | 0.5 |

Table 2 Sample stored at 22° C

| Parameter | Unit | Std deviation | Days after start of sampling 3 | 16 | 33 | 63 |
|---|---|---|---|---|---|---|
| Total ion concentration | µe/L | ± 2 | 88. | 89. | 89. | 94. |
| Conductivity | µmhos/cm | ± 0.2 | 31.2 | 29. | 31.7 | 34. |
| Hydrogen | µe/L | ± 2 | 68. | 62. | 64. | 70. |
| Sulfate | µe/L | ± 2 | 60. | 62. | 62. | 65. |
| Ammonium | µe/L | ± 1.4 | 18.6 | 20. | 17.1 | 16.4 |
| Nitrate | µe/L | ± 2 | 17. | 19. | 21. | 28. |
| Chloride | µe/L | ± 2 | 5. | 6. | 5. | 2. |
| Calcium | µe/L | ± 0.5 | 5.5 | 5.5 | 6. | 5. |
| Magnesium | µe/L | ± 0.8 | 0.8 | 0.8 | 0.8 | 0.8 |
| Sodium | µe/L | ± 0.4 | 0.4 | 0.9 | 0.9 | 0.4 |
| Potassium | µe/L | ± 0.3 | 0.8 | 1.0 | 1.0 | 0.5 |

## 4. DISCUSSION

The results show that on the whole the ion concentrations remain relatively stable through the 33rd day after sample collection began. Between the 33rd day and the 63rd day, however, the nitrate-ion concentration increases by 11 μe/L in the sample stored at $5^{o}$ C and by 7 μe/L in the sample stored at $22^{o}$ C, which is clearly unacceptable, given the initial concentrations. Since there is no corresponding decrease in the ammonium-ion concentration, the likely cause would be dissolution of nitrogenous particulates in the sample. This hypothesis receives support from the decreases in hydrogen-ion concentration and conductivity between the 3rd and 16th days and the increases in these parameters between the 16th and 63rd days.

These observations indicate that the time between the start of sample collection and the analysis should be kept to a minimum, expecially since this experiment used only one type of sample, which is not representative of all the samples collected in the Quebec precipitation program. In this program, samples are collected over 7 days, so we decided that no more than 7 additional days should be allowed for shipping and analysis of the samples. This makes a total of 14 days between the start of sample collection and the completion of the analyses.

Automatic precipitation collectors minimize particulates in the samples. Moreover, our work with various filters and filtering units has indicated an excessive risk of contaminating samples during filtration. We have therefore decided not to filter the samples before analysis, except for those that visibly require it.

Though stability of ion concentrations was nearly identical for the samples stored at the two different temperatures, we have decided to store our samples at $5^{0}$ C. We have also decided to use 8-ounce polypropylene bottles for shipping and storing our acid-precipitation samples, because our microbiology department orders 3 000 to 4 000 such bottles every year in any case. We take the bottles when they are first received, rinse them with demineralized water before using them for the precipitation samples, and later pass them on to the microbiology department.

# V

# INTERFERENCES IN ION-EXCHANGE METHODS I-A TO I-D

To test the performance of the ion-exchange columns with various electrolytes, we used the four methods described in this text to analyse 100-µe/L solutions of twelve salts composed of cations and anions usually present in all types of water. A standard containing equal concentrations of ammonium sulfate and nitric acid was analysed at the same time. The results are given in table 1.

TABLE 1

| Electrolyte | Method I-A % recovery A* | B** | Method I-B % recovery A* | B** | Method I-C % recovery A* | B** | Method I-D % recovery A* | B** |
|---|---|---|---|---|---|---|---|---|
| $(NH_4)_2\ SO_4$ | 96 | 100 | 100 | 100 | 100 | 100 | 98 | 100 |
| $Na_2SO_4$ | 100 | 100 | 100 | 100 | 100 | 100 | 98 | 100 |
| $CuSO_4$ | 98 | 100 | 99 | 100 | 99 | 100 | 99 | 100 |
| $CaSO_4$ | 102 | 100 | 101 | 100 | 101 | 100 | 100 | 100 |
| $MgSO_4$ | 100 | 100 | 98 | 100 | 98 | 100 | 98 | 100 |
| $H_2SO_4$ | 4 | 0 | 102 | 100 | 100 | 100 | 98 | 100 |
| KCl | 97 | 100 | 100 | 100 | 0 | 0 | 1 | 0 |
| NaCl | 98 | 100 | 100 | 100 | 0 | 0 | 1 | 0 |
| $CaCl_2$ | 98 | 100 | 99 | 100 | 0 | 0 | 1 | 0 |
| $MgCl_2$ | 97 | 100 | 98 | 100 | 0 | 0 | 1 | 0 |
| $KNO_3$ | 97 | 100 | 100 | 100 | 100 | 100 | 2 | 0 |
| $HNO_3$ | 4 | 0 | 100 | 100 | 100 | 100 | 2 | 0 |
| $HaHCO_3$ | 97 | 100 | 2 | 0 | 2 | 0 | 1 | 0 |

* A = actual

** B = theoretical

The results for method I-A show that the column absorbs only 96 % of the hydrogen ions, but the importance of this incomplete absorption is limited, because the calibration standard also contains an acid. The three other methods all provide acceptable recovery, and require no corrections.

Among the anions not determined by these methods, fluoride and phosphate are the ones most likely to cause interferences. Table 2 shows results for two standards containing these anions. The concentrations for the first five parameters listed were calculated as described in section II.

TABLE 2

| Determination of concentration in µe/L | Standards | |
|---|---|---|
| | $Na_3PO_4 \cdot 12H_2O$ 100 µe/L | NaF 100 µe/L |
| Hydrogen ($H^+$) | 0 | 0 |
| Total alkaline ions | 71 | 12 |
| Chloride | 0 | 0 |
| Nitrate | 0 | 60 |
| Sulfate | 29 | 28 |
| Total ions | 100 | 100 |

The analysis of the phosphate standard shows total alkalinity accounting for 71 % of its ionic composition. But this cannot be considered an interference, because phosphates, just like the alkaline ions $OH^-$, $CO_3^{--}$, and $HCO_3^-$, are titrated by an acid and are therefore an integral part of total alkalinity.

The analysis for the fluoride standard, on the other hand, shows that 100 μe/L of fluoride will increase a nitrate determination by 60 μe/L, which is enough to require a correction. In general, fluoride concentrations in precipitation samples are very low (≤0.04 mg/L) and will not interfere with nitrate determinations. But if fluorides are found in concentrations exceeding 0.05 mg/L, the results for nitrates should be corrected as follows: $NO_3^-$ in μe/L = calculated $NO_3^-$ in μe/L - 32($F^-$ in mg/L).

In sulfate determinations, fluorides and phosphates cause relatively little interference, and no correction is required for precipitation samples.

The silica naturally present in water is undissociated and therefore will not interfere with the ion-exchange determinations.

# VI

# COMPUTER OUTPUTS FOR PRECIPITATION ANALYSES

## 1. ANALYTICAL RESULTS

The computer program we have developed (see appendix I) performs the calculations described in section II, provides results for the anions and cations both in mg/L and in µe/L, computes the sum of the constituents, and calculates pH by the two methods described in section III. Results for nitrate and nitrite and for ammonia are conventionally expressed as mg/L nitrogen, so the program provides such results in this form as well.

## 2. QUALITY-CONTROL DATA

Page 69 is an example of the print-out the program provides for the analysis of a precipitation sample.* This print-out includes various data for assessing the accuracy of the analysis.

### 2.1 Anion-cation balance

The accuracy of a complete analysis of major ions can be assessed by comparison of the sum of the anions in µe/L with the sum of the cations in µe/L. If the difference between these sums does not fall within acceptable limits, one or more of the results may be invalid.

### 2.2 Comparison of measured pH with pH calculated from hydrogen-ion concentration

The program uses the method given on page 50 to calculate the pH of the sample from the hydrogen-ion concentration found in the analysis. The pH value thus calculated may be compared with the measured pH to validate the hydrogen-ion determination.

---

* The print-out has been translated here for the reader's convenience; the actual print-outs are available only in French.-tr.

## 2.3 Comparison of measured conductivity with calculated conductivity

Compensating errors in the determinations of the anions and cations may cause their sums to agree even though the individual analytical results are not really accurate. Hence an additional check is necessary. Conductivity values may serve this purpose, since they reflect the concentrations of all the ions in a solution.

The limiting conductance of a sample can be readily determined by summing the limiting conductances of all the ions in solution. In calculating the conductivity of the sample from its limiting conductance, however, a correction must be made for ionic interaction, which causes the equivalent conductance of aqueous solutions to decrease as their concentration increases. Our laboratory has developed the following formula, which incorporates such a correction and has been tested successfully on more than 3 000 samples with concentrations ranging from 0.05 to 1 000 me/L;

$$\Lambda_c = \left[ \Lambda_o^{1/k} - \left( \pi - \frac{\Lambda_o}{1000} \right) \log \left( 1 + \pi \left( \frac{C}{1000} \right) .5 \right) \right]^k$$

Where:

$\Lambda_c$ = Calculated equivalent conductance;

$\Lambda_o$ = Limiting equivalent conductance:

C = Ion concentration, in me; and

k = Ionic-interaction correction factor

## 2.4 Comparison of measured pH with pH calculated from limiting conductance and total ion concentration

The computer program uses equation 6 on page 53 to calculate the pH of the sample from its limiting conductance and total ion concentration. We will be comparing pH values thus calculated with measured pH values to further test the validity of this equation.

## PRECIPITATION ANALYSIS: RESULTS AND QUALITY CONTROL

SAMPLE # 54016. ANALYSED ON 81-07-28

**********

| CATIONS | MG/L. | MICRO EQ/L. | ANIONS | MG/L. | MICRO EQ/L. |
|---|---|---|---|---|---|
| CALCIUM | .38 | 19.0 | BICAR. | <0.1 | <2 |
| MAGNESIUM | .05 | 4.1 | CHLORIDE | .5 | 14 |
| SODIUM | .33 | 14.4 | SULFATE | 3.4 | 71 |
| POTASSIUM | .12 | 3.1 | NITRATE | 1.8 | 29 |
| AMMONIUM | .44 | 24.3 | FLUORIDE | <.02 | <1 |
| HYDROGEN | .050 | 50 | | | |
| SUM | 1.368 | 115 | | 5.70 | 114 |

SUM OF CONSTITUENTS= 7.07

AVERAGE CONCENTRATION IN MICRO EQ/L = 114.4

**********

(NO2+NO3) MG/L AS (N) = .41
NH3 MG/L AS (N) = .34
TOT. ALKALINITY (MG/L CaCO3) = <0.1

**********

| | MEASURED | CALCULATED |
|---|---|---|
| *PH | 4.29 | 4.31 |
| *CONDUCTIVITY MICROMHOS/CM | 29.7 | 30.0 |

**********

LIMITING CONDUCTANCE IN MICROMHOS/CM AT 25 C = 30.3

IONIC STRENGTH (MOLES)= .00016

[LIMITING CONDUCTANCE -0.14C]/0.287 =H+=50 PH= 4.31

**********

VII

# LIST OF METHODS USED FOR ANALYSIS OF ACID PRECIPITATION

| Parameter | Method | Unit | Detection limit | Method described in text |
|---|---|---|---|---|
| Electrical conductivity | Automated measurement with Technicon components and Radiometer conductivity meter; temperature maintained at 25° C with temperature-stabilizing bath | µmhos/cm | 0.2 | No |
| pH | A. Electrometric<br>B. Calculation (2 types) | pH unit | - | Yes |
| Acidity | Ion exchange with conductometric detection | µe/L | 2 | Yes |
| Total alkalinity | Ion exchange with conductometric detection | µe/L | 2 | Yes |
| Chloride | Ion exchange with conductometric detection | µe/L | 2 | Yes |
| Nitrates and nitrites | Ion exchange with conductometric detection | µe/L | 2 | Yes |
| Sulfate | Ion exchange with conductometric detection | µe/L | 2 | Yes |
| Total ion concentration | Ion exchange with conductometric detection | µe/L | 2 | Yes |
| Fluoride | Automated alizarin colorimetry | µe/L | 1 | No |
| Ammonium | Automated colorimetry using Berthelot reaction | µe/L | 1.4 | No |

| Parameter | Method | Unit | Detection limit | Method described in text |
|---|---|---|---|---|
| Calcium | Atomic absorption | µe/L | 0.5 | No |
| Magnesium | Atomic absorption | µe/L | 0.8 | No |
| Sodium | Atomic absorption | µe/L | 0.4 | No |
| Potassium | Atomic absorption | µe/L | 0.3 | No |

# VIII

# REFERENCES

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# APPENDIX I

## COMPUTER PROGRAM FOR ION-EXCHANGE ANALYSES OF PRECIPITATION

The program used to process the data from the precipitation analyses is written in LAB BASIC and run on a Hewlett-Packard 21 MX-E computer with a 64K memory. The program itself uses 5078 words of memory. The inputs are made on a Hewlett-Packard 2645A CRT, and the print-outs are produced on a Hewlett-Packard 2635A printer.

Note that the code ESC on lines 1710, 1725, and 2114 is specific to the 2635A printer and may be omitted without affecting the program.

TRANSLATOR'S NOTE: In the following print-out of the program, the remarks and certain commands that appear only in French in the actual program have been translated into English for the reader's convenience.

```
 2  INDVC "T1",0
 3  REM
 4  REM                          PRECIPITATION ANALYSIS:
 5  REM                        RESULTS AND QUALITY CONTROL
 6  REM
 7  LET Z$="**********************************************************************
 8  DIM Z$[65]
11   LET C$="          "
12   PRINT "DATE";
13   INPUT C$
15   PRINT "LABORATORY #";
16   INPUT X7
20   PRINT "TOTAL C - H+ ";
30   INPUT X1
50   PRINT "TOTAL C - HCO3 ";
60   INPUT X2
80   PRINT "TOTAL C - HCO3 - CL ";
90   INPUT X3
92   PRINT "TOTAL C - HCO3 - CL - NO23 ";
94   INPUT X4
110   PRINT "CONDUCTIVITY IN MICROMHOS, 25 DEG. C. ";
120   INPUT C1
130   PRINT "FLUORIDE ";
140   INPUT D7
150   LET N0=((X3-X4)-(32*D7))/71.4559
160   LET N3=N0*4.43
180   REM D4=SULFATE
190   LET D4=X4/20.82
240   PRINT "NH4, EN MG/L. DE N ";
250   INPUT N2
260   LET N5=N2*1.288
280   PRINT "CALCIUM ";
290   INPUT A6
310   PRINT "MAGNESIUM ";
320   INPUT B1
340   PRINT "SODIUM ";
350   INPUT B6
370   PRINT "POTASSIUM ";
380   INPUT B5
400   PRINT "MEASURED pH ";
410   INPUT P2
420   LET A$="(0.01"
430   LET B$="(0.001"
450   REM
460   REM                  HYDROGEN-ION CONCENTRATION
470   REM
480   LET B[10]=X2-X1
490   IF X2-X1<0 THEN 510
500   LET B[10]=(X2-X1)/1000
510   PRINT
512   REM
```

```
 515  REM           SUM OF CATIONS IN MICROEQUIVALENTS/L
 517  REM
 520  LET W1=A6*49.9
 530  LET W2=B1*82.24
 540  LET W3=B6*43.5
 550  LET W4=B5*25.58
 560  LET W5=N5*55.43
 570  LET W6=B[10]*1000
 580  IF W6<0 THEN  LET W6=0
 590  LET E=W1+W2+W3+W4+W5+W6
 600  PRINT
 610  LET D2=X1-X2
 620  IF D2<0 THEN 640
 630  LET D2=(X1-X2)/16.39
 640  PRINT
 650  LET D3=(X2-X3)/28.2
 660  REM
 670  REM             SUM OF ANIONS IN MICROEQUIVALENTS/L
 680  REM
 690  LET V1=D2*16.39
 700  IF V1<0 THEN  LET V1=0
 710  LET V2=D3*28.2
 720  LET V3=D4*20.82
 730  LET V4=N3*16.13
 740  LET V5=D7*52.63
 750  LET F=V1+V2+V3+V4+V5
 760  REM
 770  REM                   SUM OF CATIONS IN MG/L
 780  REM
 790  LET H=A6+B1+B6+B5+N5
 800  LET B9=B[10]
 810  IF B9<0 THEN  LET B9=0
 820  LET H=H+B9
 830  REM
 840  REM                   SUM OF ANIONS IN MG/L
 850  REM
 860  LET J=D3+D4+N3+D7
 870  LET B8=D2
 880  IF B8<0 THEN  LET B8=0
 890  LET J=J+B8
 900  REM
 910  REM                   SUM OF CONSTITUENTS
 920  REM
 930  LET Z=H+J
 940  REM
 950  REM           CALCULATED CONCENTRATION IN MICRO EQ./L
 960  REM
 970  LET T5=(E+F)/2
1030  REM
1040  REM                     CALCULATED pH
1050  REM
1060  IF B[10] <= 0 THEN  LET P$=">5.70"
```

```
 1070  IF B[10] <= 0 THEN 1150
 1080  LET P1=-.43429*LOG(B[10]/1000)
 1140  REM
 1150  REM                  LIMITING CONDUCTANCE
 1155  REM
 1170  LET C[1]=(A6*2.994)+(B1*4.443)+(B6*2.214)
 1180  LET C[2]=(B5*1.906)+(N5*4.13)+(D3*2.129)
 1190  LET C[3]=(D4*1.645)+(N3*1.139)+(D7*2.754)
 1200  LET C[4]=(B9*350)+(B8*.713)
 1210  LET C2=C[1]+C[2]+C[3]+C[4]
 1220  REM
 1230  REM                       K FACTOR
 1240  REM
 1250  LET H[1]=(W1/500)+(W2/500)+(W3/1000)
 1260  LET H[2]=(W4/1000)+(W5/1000)+B9
 1270  LET H6=H[1]+H[2]
 1280  LET H[3]=(V2/1000)+(V3/500)+(V4/1000)
 1290  LET H[4]=(V5/1000)+(B8*1.63900E-02)
 1300  LET H7=H[3]+H[4]
 1310  LET B7=H6/E
 1320  LET V9=H7/F
 1330  LET H[5]=2*B7*1000*V9*1000
 1340  LET H[6]=(B7*1000)+(V9*1000)
 1350  LET C4=2^(H[5]/H[6])
 1400  REM
 1410  REM          LIMITING EQUIVALENT CONDUCTANCE
 1420  REM
 1430  LET C8=(C2*1000)/T5
 1440  REM
 1450  REM          CALCULATED EQUIVALENT CONDUCTANCE
 1460  REM
 1470  LET Y1=C8^(1/C4)
 1480  LET Y2=3.14159-(C8/1000)
 1490  LET H[7]=(T5/1.00000E+06)^.5
 1500  LET Y3=.43429*LOG(1+(3.14159*H[7]))
 1510  LET C5=(Y1-(Y2*Y3))^C4
 1520  REM
 1530  REM              CALCULATED CONDUCTIVITY
 1540  REM
 1550  LET C6=(C5*T5)/1000
 1600  REM
 1610  REM                    IONIC STRENGTH
 1620  REM
 1630  LET K2=(H6+H7)/2000
 1680  REM
 1690  REM ********************** REPORT ***************** *****
 1692  REM
 1695  OUTDVC "T2",Q
 1700  PRINT TAB(15);
 1710  PRINT "&dD";"PRECIPITATION ANALYSIS:";"&d@"
 1720  PRINT TAB(18);
```

```
 1725  PRINT "ESC&dD";"RESULTS AND QUALITY CONTROL ";"ESC&d@"
 1730  PRINT
 1740  PRINT
 1750  PRINT "SAMPLE #'      ";X7;TAB(45);"ANALYSED ON ";C$
 1760  PRINT
 1771  PRINT Z$
 1773  PRINT
 1775  GOTO 2120
 1780  PRINT "SUM OF CONSTITUENTS= ";INT(Z*100+.5)/100
 1790  PRINT
 1800  PRINT "AVERAGE CONCENTRATION IN MICRO EQ/L = ";INT(T5*10+.5)/10
 1805  PRINT
 1810  PRINT Z$
 1811  PRINT
 1812  PRINT "(NO2+NO3) MG/L  AS (N)        =";
 1813  LET F[2]=2
 1814  LET F[1]=N0
 1815  GOSUB 9000
 1816  PRINT F$
 1818  PRINT "NH3        MG/L  AS (N)        =";
 1820  LET F[1]=N2
 1822  GOSUB 9000
 1824  PRINT F$
 1825  PRINT "TOT. ALKALINITY (MG/L CaCO3) =";
 1827  IF D2<.1 THEN  PRINT "   <0.1"
 1828  IF D2<.1 THEN 1833
 1829  LET F[2]=1
 1830  LET F[1]=D2/1.219
 1831  GOSUB 9000
 1832  PRINT F$
 1833  PRINT
 1835  PRINT Z$
 1836  PRINT
 1838  PRINT TAB(20);"  MEASURED     ";TAB(40);"   CALCULATED   "
 1840  PRINT TAB(20);"==============";TAB(40);"================"
 1845  PRINT
 1846  LET F[2]=2
 1850  PRINT "*PH";
 1851  LET F[1]=P2
 1852  GOSUB 9000
 1853  PRINT TAB(25);F$;
 1854  IF B[10] <= 0 THEN  PRINT TAB(45);P$
 1855  IF B[10] <= 0 THEN 1950
 1860  LET F[1]=P1+(.5*(K2^.5))
 1865  LET F[2]=2
 1870  LET F[3]=6
 1880  GOSUB 9000
 1890  PRINT TAB(45);F$
 1950  PRINT "*CONDUCTIVITY"
 1952  LET F[2]=1
 1954  LET F[1]=C1
 1955  IF C1>50 THEN  LET F[2]=0
```

```
 1956  GOSUB 9000
 1958  PRINT " MICROMHOS/CM";TAB(25);F$;
 1961  LET F[1]=C6
 1962  LET F[2]=1
 1963  GOSUB 9000
 1964  PRINT TAB(45);F$
 1965  PRINT
 1970  PRINT Z$
 1980  PRINT
 1990  PRINT "LIMITING CONDUCTANCE IN MICROMHOS/CM AT 25 C = ";
 1992  LET F[1]=C2
 1994  GOSUB 9000
 1996  PRINT F$
 2000  PRINT
 2040  PRINT "IONIC STRENGTH (MOLES)= ";
 2050  LET F[1]=K2
 2055  LET F[2]=5
 2057  LET F[3]=7
 2060  GOSUB 9000
 2070  PRINT F$
 2080  PRINT
 2088  LET W7=(C2-(.14*T5))/.287
 2089  IF W7 <= 0 THEN 2095
 2090  LET W8=(-.43429*LOG(W7/1.00000E+06))+(.5*(K2^.5))
 2093  GOTO 2097
 2095  PRINT "[LIMITING CONDUCTANCE- 0.14C]/0.287 = H+ =(1        pH)5.70"
 2096  GOTO 2104
 2097  PRINT "[LIMITING CONDUCTANCE -0.14C/0.287 =H+=";INT(W7+.5);
 2098  PRINT TAB(45);"PH= ";
 2099  LET F[2]=2
 2100  LET F[1]=W8
 2101  GOSUB 9000
 2103  PRINT F$
 2104  PRINT
 2105  PRINT Z$
 2114  PRINT "&11V"
 2115  STOP
 2120  PRINT TAB(3);"CATIONS";TAB(13);"MG/L.";TAB(23);"MICRO";
 2130  PRINT TAB(33);"ANIONS";TAB(43);"MG/L.";TAB(53);"MICRO"
 2140  PRINT TAB(23);"EQ/L.";TAB(53);"EQ/L."
 2150  PRINT TAB(3);"=======";TAB(13);"=====";TAB(23);"=====";
 2160  PRINT TAB(33);"=======";TAB(43);"=====";TAB(53);"====="
 2170  PRINT
 2175  PRINT TAB(3);"CALCIUM";
 2176  LET F[2]=2
 2177  LET F[3]=6
 2180  IF A6=0 THEN  PRINT TAB(14);"(.01";TAB(24);"(0.5";
 2185  IF A6=0 THEN 2200
 2186  LET F[1]=A6
 2189  GOSUB 9000
 2190  PRINT TAB(12);F$;
```

```
 2192  LET F[2]=1
 2194  LET F[1]=W1
 2196  GOSUB 9000
 2198  PRINT TAB(22);F$;
 2200  PRINT TAB(33);"BICAR.";
 2210  IF D2 <= 0 THEN  PRINT TAB(44);"<0.1";TAB(54);"<2"
 2215  IF D2 <= 0 THEN 2230
 2217  LET F[2]=1
 2220  LET F[1]=D2
 2222  GOSUB 9000
 2224  PRINT TAB(42);F$;TAB(54);INT(V1+.5)
 2230  PRINT
 2240  PRINT TAB(3);"MAGNESIUM";
 2245  LET F[2]=2
 2250  IF B1=0 THEN  PRINT TAB(14);"<.01";TAB(24);"<0.8";
 2255  IF B1=0 THEN 2270
 2256  LET F[1]=B1
 2258  GOSUB 9000
 2260  PRINT TAB(11);F$;
 2262  LET F[2]=1
 2264  LET F[1]=W2
 2266  GOSUB 9000
 2268  PRINT TAB(22);F$;
 2270  PRINT TAB(33);"CHLORIDE";
 2275  LET F[2]=1
 2277  LET F[1]=D3
 2278  GOSUB 9000
 2280  IF D3<9.99990E-02 THEN 2290
 2286  PRINT TAB(42);F$;TAB(54);INT(V2+.5)
 2288  GOTO 2300
 2290  IF V2<2 THEN 2296
 2292  PRINT TAB(44);"<0.1";TAB(54);INT(V2+.5)
 2294  GOTO 2300
 2296  PRINT TAB(44);"<0.1";TAB(54);"<2"
 2300  PRINT
 2310  PRINT TAB(3);"SODIUM";
 2315  LET F[2]=2
 2320  IF B6=0 THEN  PRINT TAB(14);"<.01";TAB(24);"<0.4";
 2325  IF B6=0 THEN 2340
 2326  LET F[1]=B6
 2328  GOSUB 9000
 2330  PRINT TAB(12);F$;
 2332  LET F[2]=1
 2334  LET F[1]=W3
 2336  GOSUB 9000
 2338  PRINT TAB(22);F$;
 2340  PRINT TAB(33);"SULFATE";
 2345  LET F[2]=1
 2350  IF D4=0 THEN  PRINT TAB(44);"<.2";TAB(54);"<4"
 2355  IF D4=0 THEN 2370
 2360  LET F[1]=D4
 2362  GOSUB 9000
 2364  PRINT TAB(42);F$;TAB(54);INT(V3+.5)
 2370  PRINT
 2380  PRINT TAB(3);"POTASSIUM";
 2385  LET F[2]=2
```

```
2390  IF B5=0 THEN  PRINT TAB(14);"(.01";TAB(24);"(0.3";
2395  IF B5=0 THEN 2410
2396  LET F[1]=B5
2398  GOSUB 9000
2400  PRINT TAB(11);F$;
2402  LET F[2]=1
2404  LET F[1]=W4
2406  GOSUB 9000
2408  PRINT TAB(22);F$;
2410  PRINT TAB(33);"NITRATE";
2415  LET F[2]=1
2420  IF N3=0 THEN  PRINT TAB(44);"(0.1";TAB(54);"(1"
2425  IF N3=0 THEN 2440
2430  LET F[1]=N3
2432  GOSUB 9000
2434  PRINT TAB(42);F$;TAB(54);INT(V4+.5)
2440  PRINT
2445  LET F[2]=2
2450  PRINT TAB(3);"AMMONIUM";
2455  LET F[2]=2
2460  IF N5=0 THEN  PRINT TAB(14);"(.01";TAB(24);"(0.6";
2465  IF N5=0 THEN 2480
2466  LET F[1]=N5
2468  GOSUB 9000
2470  PRINT TAB(12);F$;
2472  LET F[2]=1
2474  LET F[1]=W5
2476  GOSUB 9000
2478  PRINT TAB(22);F$;
2480  PRINT TAB(33);"FLUORIDE";
2490  IF D7=0 THEN  PRINT TAB(44);"(.02";TAB(54);"(1"
2495  IF D7=0 THEN 2510
2496  LET F[1]=D7
2497  LET F[2]=2
2498  GOSUB 9000
2500  PRINT TAB(35);F$;TAB(54);INT(V5+.5)
2510  PRINT
2520  PRINT TAB(3);"HYDROGEN";
2530  IF B[10] <= 0 THEN  PRINT TAB(14);"(.001";TAB(24);"(1"
2535  IF B[10] <= 0 THEN 2550
2536  LET F[1]=B[10]
2537  LET F[2]=3
2539  GOSUB 9000
2540  PRINT TAB(11);F$;TAB(24);INT(W6+.5)
2550  PRINT
2555  PRINT
2556  PRINT TAB(3);"=====";
2557  PRINT TAB(14);"=====";TAB(24);"=====";TAB(43);"=====";
2558  PRINT TAB(53);"====="
2570  PRINT TAB(3);"SUM";
2573  LET F[1]=H
2574  LET F[3]=7
```

```
 2575  GOSUB 9000
 2580  PRINT TAB(12);F$;TAB(24);INT(E+.5);
 2582  LET F[2]=2
 2584  LET F[1]=J
 2587  GOSUB 9000
 2590  PRINT TAB(41);F$;TAB(54);INT(F+.5)
 2605  PRINT
 2607  PRINT
 2610  GOTO 1780
 9000  FOR J9=1 TO F[3]
 9001  REM
 9002  REM          FORMATTER SUBROUTINE
 9003  REM
 9005  LET F$[J9]=" "
 9010  NEXT J9
 9015  IF F[2]>F[3]-2 THEN 9180
 9020  LET F[2]=ABS(INT(F[2]+.5))
 9025  LET F$[26,35]="1234567890"
 9030  LET F[4]=F[3]-F[2]
 9035  LET F[5]=ABS(F[1])+.5*10^(-F[2])
 9040  LET F[6]=F[8]=0
 9045  IF INT(F[5])=0 THEN 9120
 9050  IF F[6]>0 THEN  LET F[5]=F[5]/10
 9055  LET F[6]=F[6]+1
 9060  IF F[6]>F[3]-F[2]-2 THEN 9180
 9065  IF INT(F[5])>9 THEN 9050
 9075  FOR J9=F[6] TO 1 STEP -1
 9080  IF INT(F[5])=0 THEN  LET F[5]=F[5]+10
 9085  LET F[8]=F[8]+1
 9090  LET F$[F[4]-J9,F[4]-J9]=F$[INT(F[5])+25]
 9095  IF F[8]>6 THEN  LET F[5]=0
 9100  LET F[5]=10*(F[5]-INT(F[5]))
 9105  NEXT J9
 9110  IF F[8]>6 THEN 9165
 9115  LET F[5]=ABS(F[1])+.5*10^(-F[2])
 9120  FOR J9=1 TO F[2]
 9125  LET F[7]=F[4]+J9
 9130  LET F[5]=10*(F[5]-INT(F[5]))
 9135  IF INT(F[5])=0 THEN  LET F[5]=F[5]+10
 9140  LET F[8]=F[8]+1
 9145  LET F$[F[7],F[7]]=F$[INT(F[5])+25]
 9150  IF F[8]>6 THEN 9160
 9155  NEXT J9
 9160  LET F$[F[4]]="."
 9165  IF F[1]<0 THEN  LET F$[F[4]-F[6]-1]="-"
 9170  LET F$[F[3]+1]=""
 9175  RETURN
 9180  FOR J9=1 TO F[3]
 9185  LET F$[J9]="$"
 9190  NEXT J9
 9195  GOTO 9170
 9200  DIM F$[35],F[8]
 9999  END
```